H_4-An′ together with a mixture of ruthenium products, including $[RuH_2(PPh_3)_3(THF)]$, $[RuH_2(PPh_3)_2(THF)_2]$ and $[RuH_2(PPh_3)_4]$, and with a small amount (0.05 equiv) of a product (δ_{Ru-H} −19.6 (J_{P-H} = 30 Hz)) tentatively identified as $[RuH_2(\eta^4\text{-An}')(PPh_3)_2]$. An analogous, η^4-complex $[RuH_2(\eta^4\text{-DPB})(PPh_3)_2]$ (DPB = *trans,trans*-1,4-diphenylbutadiene) was obtained in ca. 30% yield by reacting $[RuH_4(PPh_3)_3]$ with DPB in THF-d_8 at 25 °C according to eq 13.

$$[RuH_4(PPh_3)_3] + 0.9\,\mathrm{DPB} \rightarrow 0.33[RuH_2(PPh_3)_3(THF)] + 0.33[RuH_2(PPh_3)_4] + 0.33[RuH_2(\eta^4\text{-DPB})(PPh_3)_2] + 0.5[1,4\text{-diphenylbutane}] \quad (13)$$

$[RuH_2(\eta^4\text{-DPB})(PPh_3)_2]$ also was prepared by protonation of $[RuH(\eta^4\text{-DPB})(PPh_3)_2]^-$ [4] with 1 equiv of H_2O although this reaction also produces some unidentified products. The NMR spectrum of $[RuH_2(\eta^4\text{-DPB})(PPh_3)_2]$ suggests two nonequivalent phosphorus atoms and two equivalent hydrogens: ^1H NMR δ −11.9 (dd, J_{P-H} = 27 Hz, $J_{P'-H}$ = 23 Hz, 2 H, RuH_2); $^{31}P\{^1H\}$ NMR δ 67.0 (d, P_{P-P} = 80 Hz, 1 P), δ 59.5 (d, 1P); each signal splits into the expected doublet of triplets upon selective decoupling of the aryl protons. $[RuH_2(\eta^4\text{-DPB})(PPh_3)_2]$ was found to be unreactive toward H_2 and thus does not appear to be a catalytic intermediate.

Reaction of $[RuH_4(PPh_3)_3]$ with an excess (ca. 4 equiv) of An′ resulted in formation, after ca. 4 h at 65 °C, of 1 equiv of H_4-An′ implying reduction of the ruthenium to Ru(0), possibly to $[Ru(\eta^4\text{-An}')(PPh_3)_3]$ or $[Ru(\eta^6\text{-An}')(PPh_3)_2]$. Analogues of both species have previously been reported, namely, $[Ru(\eta^4\text{-}C_4H_6)(PPh_3)_3]$[18] and $[Os(\eta^6\text{-}C_6H_6)(PPh_3)_2]$.[19]

We have confirmed earlier reports[18] that $[RuH_4(PPh_3)_3]$ reacts with dienes, for example, 1,3-butadiene to form (after ca. 20 min at room temperature in C_6D_6) $[Ru(\eta^4\text{-}C_4H_6)(PPh_3)_3]$ (eq 14). The latter reacts more slowly (ca. 1.5 h) with more butadiene to form $[Ru(\eta^4\text{-}C_4H_6)_2(PPh_3)]$ (eq 15) [$^{31}P\{^1H\}$ NMR δ 67.9 ppm (br s)]. $[Ru(\eta^4\text{-}C_4H_6)(PPh_3)_3]$ reacts rapidly with H_2 to regenerate $[RuH_4(PPh_3)_3]$. Equations 14 and 16 constitute a catalytic cycle for the hydrogenation of butadiene. On the other hand, $[Ru(\eta^4\text{-}C_4H_6)_2(PPh_3)]$ was found to be unreactive toward H_2 (or even toward PPh_3) and, thus, represents an unproductive dead end.

$$[RuH_4(PPh_3)_3] + 2[1,3\text{-}C_4H_6] \rightarrow [Ru(\eta^4\text{-}C_4H_6)(PPh_3)_3] + C_4H_{10} \quad (14)$$

$$[Ru(\eta^4\text{-}C_4H_6)(PPh_3)_3] + 1,3\text{-}C_4H_6 \rightarrow [Ru(\eta^4\text{-}C_4H_6)_2(PPh_3)] + 2PPh_3 \quad (15)$$

$$[Ru(\eta^4\text{-}C_4H_6)(PPh_3)_3] + 4H_2 \rightarrow [RuH_4(PPh_3)_3] + C_4H_{10} \quad (16)$$

Concluding Remarks

These studies have revealed that $[RuH_4(PPh_3)_3]$ is an effective and versatile catalyst for the hydrogenation of ketones and arenes and have served to elucidate some aspects of the mechanisms of these reactions and to identify and characterize some of the intermediates. In comparative studies we have failed to identify any distinctive properties or advantages of the anionic catalyst $[RuH_3(PPh_3)_3]^-$, over the related neutral complex $[RuH_4(PPh_3)_3]$, for the hydrogenation either of ketones or of arenes. Indeed, the latter was found to be the more effective catalyst for both reactions.

Acknowledgment. Support of this research through a grant from the National Science Foundation and a generous loan of ruthenium from Johnson, Matthey, Inc., is gratefully acknowledged. The NMR facilities used in the research were supported in part through the University of Chicago Cancer Center Grant No. NIH-CA-14599.

---

(19) Werner, H.; Werner, R. *J. Organomet. Chem.* **1980**, *194*, C7.

Highly Stabilized Copper(III) Complexes

Fred C. Anson, Terrence J. Collins,*[1] Thomas G. Richmond, Bernard D. Santarsiero, James E. Toth, and Brian G. R. T. Treco

Contribution No. 7450 from The Chemical Laboratories, The California Institute of Technology, Pasadena, California 91125. *Received July 30, 1986*

Abstract: It has been possible to synthesize a family of copper complexes in the rare +III oxidation state by employing strongly donating polyanionic chelating (PAC) ligands containing organic *N*-amido and oxido donors. The X-ray crystal structure of one example, $[PPh_4][Cu(\eta^4\text{-}\mathbf{4})]\cdot 2H_2O$ ($H_4\mathbf{4}$ = 1,2-bis(2-hydroxy-2-methylpropanamido)benzene), is reported. The metal center is found in a square-planar environment with normal bond distances and angles for the copper(III) formulation. Copper(III/II) couples are highly sensitive to ligand environments. This property is exploited to assess the relative donor properties of a series of PAC ligands containing *N*-amido, phenolato, and alkoxido donors. The possible noninnocence of the PAC ligands that contain aromatic groups is considered, and an approach for determining the best formal oxidation state assignments for the metal centers in potentially ambiguous cases is introduced. The trend in formal potentials as the aromatic groups of the PAC ligands are replaced by aliphatic groups indicates that oxidation of each copper(II) complex is metal-centered. The formal potentials of the copper(III/II) couples vary over a range of more than 1.1 V (−1.08 to +0.14 V vs. Fc^+/Fc). Alkoxide ligands are much stronger donors than phenoxide ligands. The copper(III) complexes of the more donating PAC ligands are considerably more stabilized (more negative formal potentials for copper(III/II) couples) than has been observed hitherto for complexes with first-row donor complements.

Interest in copper compounds of the rare +III oxidation state has mounted substantially in the last decade. Although few copper(III) compatible ligand environments have been discovered, a rich coordination chemistry has been developed for several systems.[2-9] A debate is in progress over the possible participation of copper(III) complexes in certain enzymatic processes.[10] In the specific case of galactose oxidase one side has copper(III) as

---

(1) Dreyfus Teacher-Scholar, 1986–1990. Alfred P. Sloan Research Fellow, 1986–1988.

0002-7863/87/1509-2974$01.50/0

the catalytically active species, a two-electron oxidant that converts an alcohol to an aldehyde.[10] There is a need for additional stable copper(III) compounds for biomimetic studies, and in this report we show that a series of polyanionic chelating (PAC) ligands containing *N*-amido and oxido donors[11-14] is a source of a new family of copper(III) complexes. As a further matter of general interest the copper(III/II) couple provides an excellent analytical tool for assessing the relative donor capacities of ligand complements. Margerum and co-workers have demonstrated that copper(III/II) couples span a wide range of formal potentials depending upon the σ-donor capacities of the ligand complements (the HOMO's of the copper(II) complexes have σ^* symmetry).[2] As ligand donor features significantly determine the oxidizing properties of inorganic complexes, an understanding of ligand donor characteristics is an important element of the design of inorganic redox systems. While at first sight the PAC ligands studied appear to be rather similar, considerable differences in donor capacities are evident as the formal potentials of the copper(III/II) couples vary by over 1.1 V. Here we show that the values of the formal potentials can be used to address the normally perplexing problems of oxidation state assignments to complexes of potentially noninnocent ligands. The trend in formal potentials as the PAC ligands are systematically modified by substitution of aliphatic for aromatic groups suggests that each oxidized complex is best described as a copper(III) complex and not a ligand-oxidized copper(II) species. The copper(III) complexes of the more basic PAC ligands are considerably more stabilized (more negative formal potentials for copper(III/II) couples) than has been observed hitherto for complexes with first-row donor complements.

Experimental Section

Materials. All solvents were reagent grade (Aldrich, Baker, Malinckrodt, M.C.B., or U.S.I.) and were used as received except as described for electrochemical measurements. α-Methyl lactic acid (Aldrich), trimethylacetyl chloride (Aldrich), thionyl chloride (Baker), pyridine (Baker), triethylamine (Baker), sodium hydroxide (Baker), tetraphenylphosphonium chloride (Aldrich), tetra-*n*-butylammonium hydroxide (Aldrich), tetramethylammonium hydroxide (Aldrich), 1,2-phenylenediamine (Aldrich), 4,5-dichloro-1,2-phenylenediamine (Aldrich), sodium azide (Aldrich), ammonium sulfide (22% in water, Malinckrodt), silver acetate (Baker), and *tert*-butyl hydroperoxide (Aldrich, 90%) were used as received without further purification. Analytical and preparative thin-layer chromatography plates, 250 and 1000 μm, respectively, were silica gel GF (Analtech).

Physical Measurements. ^{1}H NMR spectra were recorded at 90 MHz on a Varian EM 390 or on a JEOL FX90-Q spectrometer. Unless otherwise noted ^{1}H shifts are reported in δ vs. Me_4Si as internal standard. IR spectra were recorded on a Beckman IR 4240 spectrophotometer. Elemental analyses were obtained at the Caltech analytical facility.

Syntheses. The ligands H_4CHBA-DCB (H_4**1**) and H_4CHBA-Et (H_4**2**) have been previously described.[14]

2-Methyl-2-(trimethylacetoxy)propanoic Acid. 2-Methyl lactic acid (30 g) and pivaloyl chloride (35.5 mL) were mixed in tetrahydrofuran (100 mL). Pyridine (36 mL, 1 equiv) was added in aliquots (3 mL). The mixture was stirred (18 h), and the precipitate was removed by filtration. The solvent was removed on a rotary evaporator, the residue was dissolved in dichloromethane and filtered, and crystallization was effected by slow removal of dichloromethane on a rotary evaporator to afford a white crystalline product which was dried at 60 °C under vacuum: yield 48 g (88.5%); ^{1}H NMR (δ, $CDCl_3$) 1.2 (s, 9 H, $(CH_3)_3C-$), 1.6 (s, 6 H, $-(CH_3)_2C-$).

2-Methyl-2-(trimethylacetoxy)propanoyl Chloride. 2-Methyl-2-trimethylacetoxy)propanoic acid (10 g) was stirred in thionyl chloride (10 mL, 18 h). The excess $SOCl_2$ was removed by distillation at atmospheric pressure under N_2. The acid chloride was distilled from the remaining oil (50–55 °C, 0.005 torr): yield 6.25 g (57%); ^{1}H NMR (δ, $CDCl_3$) 1.2 (s, 9 H, $(CH_3)_3C-$), 1.6 (s, 6 H, $-(CH_3)_2C-$); IR (cm^{-1}) ν_{CO} 1800.

1,2-Bis(2-(trimethylacetoxy)-2-methylpropamido)benzene. 2-Methyl-2-(trimethylacetoxy)propanoyl chloride (6.25 g, 29.1 mmol) was

---

(2) Bossu, F. P.; Chellappa, K. L.; Margerum, D. W. *J. Am. Chem. Soc.* **1977**, *99*, 2195–2203.

(3) (a) Owens, G. D.; Phillips, D. A.; Czarnecki, J. J.; Raycheba, J. M. T.; Margerum, D. W. *Inorg. Chem.* **1984**, *23*, 1345–1354. (b) Anast, J. M.; Hamburg, A. W.; Margerum, D. W. *Ibid.* **1983**, *22*, 2139–2145. (c) Hamburg, A. W.; Margerum, D. W. *Ibid.* **1983**, *22*, 3384–3393. (d) Margerum, D. W. *Pure Appl. Chem.* **1983**, *55*, 23–34. (e) Diaddario, L. L.; Robinson, W. R.; Margerum, D. W. *Inorg. Chem.* **1983**, *22*, 1021–1025. (f) Margerum, D. S. *Oxidases Relat. Redox Syst., Proc. Int. Symp., 3rd* **1979**. (g) Anast, J. M.; Margerum, D. W. *Inorg. Chem.* **1982**, *21*, 3494–3501. (h) Koval, C. A.; Margerum, D. W. *Ibid.* **1981**, *20*, 2311–2318. (i) Anast, J. M.; Margerum, D. W. *Ibid.* **1981**, *20*, 2319–2326. (j) Owens, G. D.; Margerum, D. W. *Ibid.* **1981**, *20*, 1146–1453. (k) Margerum, D. W.; Owens, G. D. *Met. Ions Biol. Syst.* **1981**, *12*, 75–132. (l) Raycheba, J. M. T.; Margerum, D. W. *Inorg. Chem.* **1981**, *20*, 45–51. (m) Rybka, J. S.; Margerum, D. W. *Ibid.* **1981**, *20*, 1453–1458. (n) Rybka, J. S.; Kurtz, J. L.; Neubecker, *T.* A.; Margerum, D. W. *Ibid.* **1980**, *19*, 2791–2796. (o) Margerum, D. W.; Chellappa, K. L.; Bossu, F. P.; Burce, G. L. *J. Am. Chem. Soc.* **1975**, *97*, 6894–6896.

(4) Diaddario, L. L.; Robinson, W. R.; Margerum, D. W. *Inorg. Chem.* **1983**, *22*, 1021–1025.

(5) Youngblood, M. P.; Margerum, D. W. *Inorg. Chem.* **1980**, *19*, 3068–3072.

(6) See, for example: (a) Fabbrizzi, L.; Licchelli, M.; Perotti, A.; Poggi, A.; Soresi, S. *Isr. J. Chem.* **1985**, *25*, 112–117. (b) Castellani, C. B.; Fabbrizzi, L.; Licchelli, M.; Perotti, A.; Poggi, A. *J. Chem. Soc., Chem. Commun.* **1984**, 806–808. (c) Buttafava, A.; Fabbrizzi, L.; Perotti, A.; Poggi, A.; Seghi, B. *Inorg. Chem.* **1984**, *23*, 3917–3922. (d) Fabbrizzi, L.; Forlini, F.; Perotti, A.; Seghi, B. *Inorg. Chem.* **1984**, *23*, 807–813. (e) Fabbrizzi, L.; Perotti, A.; Poggi, A. *Inorg. Chem.* **1983**, *22*, 1411–1412. (f) Buttafava, A.; Fabbrizzi, L.; Perotti, A.; Seghi, B. *J. Chem. Soc., Chem. Commun.* **1982**, 1166–1167. (g) Zanello, P.; Seeber, R.; Cinquantini, A.; Mazzocchin, G. A.; Fabbrizzi, L. *J. Chem. Soc., Dalton Trans.* **1982**, 893–897. (h) Fabbrizzi, L.; Poggi, A. *J. Chem. Soc., Chem. Commun.* **1980**, 646–647. (i) Kimura, E.; Koike, T.; Machida, R.; Nagai, R.; Kodama, M. *Inorg. Chem.* **1984**, *23*, 4181–4188. (j) Sharp, P. R.; Bard, A. J. *Inorg. Chem.* **1983**, *22*, 3462–3464. (k) Brown, D. G.; Weser, U. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1979**, *34B*, 989–994. (l) Yano, Y.; Takano, S.; Kato, Y.; Tagaki, W. *J. Chem. Soc., Perkin Trans. 2* **1979**, 1227–1229. (m) Keyes, W. E.; Dunn, J. B. R.; Loehr, T. M. *J. Am. Chem. Soc.* **1977**, *99*, 4527–4529. (n) Clark, G. R.; Skelton, B. W.; Waters, T. N. *J. Chem. Soc., Dalton Trans.* **1976**, 1528–1536. (o) Clark, G. R.; Skelton, B. W.; Waters, T. N. *J. Chem. Soc., Chem. Commun.* **1972**, 1163. (p) Bour, J. J.; Birker, P. J. M. W. L.; Steggerda, J. J. *Inorg. Chem.* **1971**, *10*, 1202–1205. (q) Olson, D. C.; Vasilevskis, J. *Inorg. Chem.* **1971**, *10*, 463–470. (r) Beurskens, P. T.; Cras, J. A.; Steggerda, J. J. *Inorg. Chem.* **1968**, *7*, 810–813. (s) Bour, J. J.; Steggerda, J. J. *Chem. Commun.* **1967**, 85. (t) Sharp, P. R.; Bard, A. J. *Inorg. Chem.* **1983**, *22*, 3462–3464.

(7) Warren, L. F.; Bennett, M. A. *Inorg. Chem.* **1976**, *15*, 3126–3140.

(8) (a) Sulfab, Y.; Hussein, M. A.; Al-Shatti, N. I. *Inorg. Chim. Acta* **1982**, *67*, L33–L34. (b) Hendrickson, A. R.; Martin, R. L.; Rohde, N. M. *Inorg. Chem.* **1976**, *15*, 2115–2119. (c) Hollander, F. J.; Caffery, M. L.; Coucouvanis, D. *J. Am. Chem. Soc.* **1974**, *96*, 4682–4684. (d) Cinquantini, A.; Cini, R.; Seeber, R.; Zanello, P. *J. Electroanal. Chem.* **1981**, *121*, 301–309. (e) Baker-Hawkes, M. J.; Billig, E.; Gray, H. B. *J. Am. Chem. Soc.* **1966**, *88*, 4870–4875.

(9) For examples of copper(III) species being invoked in chemical reactions see: (a) Capdevielle, A. E.; Audebert, P.; Maumy, M. *Tetrahedron Lett.* **1984**, *25*, 4397–4400. (b) Cahill, A. E.; Taube, H. *J. Am. Chem. Soc.* **1952**, *74*, 2312–2318.

(10) (a) Johnson, J. M.; Halshall, H. B.; Heineman, W. R. *Biochemistry* **1985**, *24*, 1579–1585. (b) Kwiatkowski, L. D.; Adelman, M.; Pennelly, R.; Kosman, D. J. *J. Inorg. Biochem.* **1981**, *14*, 209–222. (c) Winkler, M. E.; Bereman, R. D. *J. Am. Chem. Soc.* **1980**, *102*, 6244–6247. (d) Hamilton, G. A.; Adolf, P. K.; de Jersey, J.; DuBois, G. C.; Dyrkacz, G. R. Libby, R. D. *J. A. Chem. Soc.* **1978**, *100*, 1899–1912. (e) Dyrkacz, G. R.; Libby, R. D.; Hamilton, G. A. *J. Am. Chem. Soc.* **1976**, *98*, 626–628. (f) Hamilton, G. A.; Libby, R. D.; Hartzell, C. R. *Biochem. Biophys. Res. Commun.* **1973**, *55*, 333–.

(11) (a) Anson, F. C.; Collins, T. J.; Gipson, S. L.; Keech, J. T.; Krafft, T. E.; Santarsiero, B. D.; Spies, G. H. *J. Am. Chem. Soc.* **1984**, *106*, 4460–4472. (b) Christie, J. A.; Collins, T. J.; Krafft, T. E.; Santarsiero, B. D. Spies, G. H. *J. Chem. Soc., Chem. Commun.* **1984**, 198–200. (c) Collins, T. J.; Santarsiero, B. D.; Spies, G. H. *J. Chem. Soc., Chem. Commun.* **1983**, 681–682. (d) Anson, F. C.; Collins, T. J.; Gipson, S. L.; Keech, J. T.; Krafft, T. E. *Inorg. Chem.*, in press. (e) Anson, F. C.; Collins, T. J.; Coots, R. J.; Gipson, S. L.; Keech, J. t.; Krafft, T. E. Santarsiero, B. D.; Spies, G. H. *Inorg. Chem.*, in press. (f) Anson, F. C.; Collins, T. J.; Gipson, S. L. Keech, J. T.; Krafft, T. E. *Inorg. Chem.*, in press. (g) Barner, C. J.; Collins, T. J.; Mapes, B. E.; Santarsiero, B. D. *Inorg. Chem.* **1986**, *25*, 4322–4323. (h) Collins, T. J.; Ozaki, S.; Richmond, T. G., submitted for publication in *J. Chem. Soc., Chem. Commun.*

(12) (a) Anson, F. C.; Collins, T. J.; Coots, R. J.; Gipson, S. L.; Richmond, T. G. *J. Am. Chem. Soc.* **1984**, *106*, 5037–5038. (b) Brewer, J. C.; Collins, T. J.; Smith, M. R.; Santarsiero, B. D., submitted for publication in *J. Am. Chem. Soc.*

(13) Collins, T. J.; Richmond, T. G.; Santarsiero, B. D.; Treco, B. G. R. T. *J. Am. Chem. Soc.* **1986**, *108*, 2088–2090.

(14) (a) Collins, T. J.; Coots, R. J.; Furutani, T. T.; Keech, J. T.; Peake, G. T.; Santarsiero, B. D. *J. Am. Chem. Soc.* **1986**, *108*, 5333–5339. (b) Anson, F. C.; Collins, T. J.; Gipson, S. L.; Keech, J. T.; Krafft, T. E.; Peake, G. T. *J. Am. Chem. Soc.* **1986**, *108*, 6593–6605. (c) Collins, T. J.; Lai, T.; Peake, G. T., submitted for publication in *Inorg. Chem.* (d) Collins, T. J.; Lee, S. C.; Keech, J. T., submitted for publication in *J. Am. Chem. Soc.*

dissolved in dichloromethane (25 mL) and tetrahydrofuran (50 mL). 1,2-Phenylenediamine (1.5 g, 13.9 mmol) in THF (10 mL) was added followed by triethylamine (10 mL), and the mixture was stirred (18 h). The white precipitate (Et_3NHCl) was separated by filtration, and the solvents were removed on a rotary evaporator to give a white solid: yield 6.0 g (91%); ^1H NMR (δ, $CDCl_3$) 8.2 (br s, 2 H, N–H), 7.1–7.5 (m, 4 H, C_6H_4), 1.7 (s, 12 H, $-(CH_3)_2CO-$), 1.3 (s, 18 H, $(CH_3)_3CC(O)O-$).

1,2-Bis(2-hydroxy-2-methylpropanamido)benzene H$_4$4. 1,2-Bis(2-(trimethylacetoxy)-2-methylpropanamido)benzene (11.3 g, 21 mmol) and sodium hydroxide (4 g, 100 mmol) were added to a mixture of methanol (100 mL) and ethanol (20 mL) and were heated under reflux (3 h). Analytical TLC (CH_2Cl_2/THF, 9:1) showed no starting material remained. The solvents were removed on a rotary evaporator, and the residue was dissolved in acetone (200 mL). The solvent volume was reduced to 100 mL, the mixture was filtered, and the filtrate was passed through silica gel (2 in. in 60-mL sintered glass crucible). The solvent volume was reduced to 25 mL, and dichloromethane was added to give a white solid product (4.05 g). A second crop was obtained by addition of diethyl ether to the mother liquor (1.4 g): total yield 5.45 g (88%, 80% from starting diamine); ^1H NMR (δ, Me_2SO-d_6) 9.4 (s, 2 H, N–H), 7.0–7.5 (m, 4 H, C_6H_4), 1.3 (s, 12 H, $-(CH_3)_2CO-$); IR (cm^{-1}, Nujol) ν_{CO} (amide) 1660. Anal. Calcd for $C_{14}H_{20}N_2O_4$: C, 60.02; H, 7.14, N, 9.99. Found: C, 59.65; H, 7.03; N, 9.92.

1,2-Bis(2-hydroxy-2-methylpropanamido)-3,4-dichlorobenzene, H$_4$3. This material was prepared in 48% yield in an analogous manner to the compound described above with the exception that 4,5-dichloro-1,2-phenylenediamine was used in place of 1,2-phenylene: ^1H NMR (δ, Me_2SO-d_6) 9.3–9.8 (s 2 H, N–H), 7.8 (s, 2 H, C_6H_4), 3.3–3.7 (s, 2 H, O–H), 1.3 (s, 12 H, $-(CH_3)_2CO-$); IR cm^{-1}, Nujol) ν_{co} (amide) 1665. Anal. Calcd for $C_{14}H_{18}Cl_2N_2O_4$: C, 48.17; H, 5.13; N, 8.02. Found: C, 47.85; H, 5.15,; N, 7.97.

2,4-Bis(2-hydroxy-2-methylpropanamido)-2,4-dimethyl-3-oxopentane, H$_4$5. 2,4-Diamino-2,4-dimethylpentan-3-one[15] (4.69 g, 27 mmol) and (trimethylacetoxy)isobutyryl chloride (10.83 g, 53.9 mmol) were mixed in THF (100 mL). Triethylamine (10.83 g, 53.9 mmol) was added leading to an exothermic reaction with formation of a white precipitate. The reaction mixture was stirred (18 h) and filtered. The solvent volume was reduced on a rotary evaporator to give a pale oil which was heated under reflux (12 h) in methanol (100 mL) with NaOH (0.320 g, 80 mmol). The reaction mixture was cooled, the solvents were removed on a rotary evaporator, and the residue was stirred in acetone (100 mL, 12 h). The white insoluble material (primarily sodium pivolate) was removed by filtration. The filtrate was again reduced in volume on a rotary evaporator. The oil was stirred in dichloromethane (200 mL, 1 h). An oily solid remained undissolved which was removed by filtration, and an equal volume of hexane was added to the filtrate. The solvent volume was slowly reduced on a rotary evaporator, giving the product as a white powder: yield 2.92 g (35% based on starting diamine); ^1H NMR (δ, $CDCl_3$) 7.5 (s, 2 H, N–H), 2.82 (s, 2.5 H, O–H plus residual H_2O), 1.7 (s, 12 H, $-CH_3$), 1.2 (s, 12 H, $-CH_3$); IR (cm^{-1}, Nujol) ν_{CO} (ketone) 1710, ν_{CO} (amide) 1650. Anal. Calcd for $C_{15}H_{28}N_2O_5 \cdot 0.25H_2O$: C, 56.18; H, 8.88; N, 8.73. Found: C, 56.18; H, 8.53; N, 8.67. Water solvate quantified by ^1H NMR.

[(C$_4$H$_9$)$_4$N)]$_2$[Cu(η^4-1)]. H$_4$CHBA-Et (1.00 g, 2.28 mmol) and Cu(OAc)$_2$·H$_2$O (0.45 g, 2.5 mmol) were mixed in ethanol (20 mL) and THF (20 mL), and the colorless solution with suspended copper acetate was stirred. A solution of tetrabutylammonium hydroxide in methanol (25%, 11.0 g, 42.5 mmol) was added, and the reaction immediately became an intense translucent violet. The reaction mixture was stirred (1 h) and filtered, and the solvents were removed on a rotary evaporator. The residue was treated with THF (30 mL), and a purple solid formed which was collected by filtration and dried. Upon standing a second crop separated which was also collected and dried: combined yield 2.20 g (90%). Anal. Calcd for $C_{24}H_{26}Cl_4CuN_4O$: C, 58.48; H, 8.52, N, 5.68. Found: C, 58.13; H, 8.56; N, 5.37.

[(C$_4$H$_9$)$_4$N][Cu(η^4-2)]. This complex was prepared in an analogous manner to [(C$_4$H$_9$)$_4$N]$_2$[Cu(η^4-1)], substituting the ligand H$_4$-CHBA-DCB for H$_4$-CHBA-Et in the above preparation. Anal. Calcd for $C_{28}H_{24}Cl_6CuN_4N_4O_4$: C, 56.84; H, 6.55; N, 5.10. Found: C, 56.53; H, 6.92, N, 5.17.

[(CH$_3$)$_4$N]$_2$[Cu(η^4-3)]. 1,2-Bis(2-hydroxy-2-methylpropanamido)-3,4-dichlorobenzene (0.200 g, 573 μmol) and Cu(OAc)$_2$·H$_2$O (0.115 g, 573 μmol) were mixed with [(CH$_3$)$_4$N][OH]·5H$_2$O (0.104 g, 573 μmol) in absolute ethanol (25 mL) and stirred (1 h). The reaction mixture was filtered, and the solvent was removed from the purple solution on a rotary evaporator. The remaining oil was treated with hexane to give a blue solid: yield 0.16 g (50%). A satisfactory elemental analysis was obtained for this hygroscopic compound if two waters of solvation were included in the molecular formula. However, independent verification of the solvate quantity was not obtained.

[PPh$_4$][Cu(η^4-4)]·2H$_2$O. Cu(OAc)$_2$·H$_2$O (0.160 g, 797 μmol), H$_4$HMPA-B (0.200 g, 714 μmol), and NaOH (0.120 g) were stirred in ethanol (50 mL, 1 h). Addition of solid AgOAc (0.200 g) to the deep purple solution afforded a deep red solution which was filtered through Celite to remove solids, and the solvents were removed on a rotary evaporator. Redissolution in ethanol showed that some purple color remained so the oxidation with AgOAc was repeated. The product was dissolved in H$_2$O, and addition of excess [PPH$_4$]Cl in water caused precipitation. Recrystallization from acetone/water afforded plate-like crystals: yield 0.225 g (53%). Single crystals for X-ray diffraction were obtained from acetone/water. Anal. Calcd for $C_{38}H_{40}N_2CuO_6P$: C, 63.81; H, 5.64; N, 3.92. Found: C, 63.25; H, 5.33; N, 3.97. The sodium salt can be prepared by extraction of the [PPh$_4$]$^+$ salt into aqueous solution in the presence of 1 equiv of NaClO$_4$. ^1H NMR of Na$^+$ salt (δ, acetone-d_6): 7.85 (dd, 2 H, C_6H_4), 6.75 (dd, 2 H, C_6H_4), 1.23 (s, 12 H, $-(CH_3)_2C-$).

[(CH$_3$)$_4$N][Cu(η^4-5)]. H$_4$HMPA-DMP (0.500 g, 1.58 mmol), Cu(OAc)$_2$ (0.287 g, 1.58 mmol) and [(CH$_3$)$_4$N][OH]·5H$_2$O (1.140 g, 6.3 mmol) were stirred in ethanol (50 mL, 2 h). The ethanol was removed on a rotary evaporator to leave a purple oil to which CH$_2$Cl$_2$ (50 mL) was added. The oil did not dissolve until excess tert-butyl hydroperoxide in toluene was added giving rapid formation of a red soluble product. The CH$_2$Cl$_2$ was removed on a rotary evaporator to leave a red oil which was recrystallized from CH$_2$Cl$_2$/cyclohexane to yield a red solid which was dried: yield 0.465 g (63%); ^1H NMR (δ, Me_2SO-d_6) 3.1 (s, 14.8 H, [(CH$_3$)$_4$N]$^+$ and H$_2$O), 1.6 (s, 12 H, $-(CH_3)_2C-$), 1.0 (s, 12 H, $-(CH_3)_2C-$); IR cm^{-1}, Nujol) ν_{CO} (amide)1600 ν_{CO} (ketone) 1710. Anal. Calcd for $C_{19}H_{24}CuN_3O_5 \cdot 1.4H_2O$ (solvate quantified by ^1H NMR): C, 48.33, H, 7.81; N, 9.14. Found: C, 48.04; 8.16, N, 8.84.

Crystal data for [PPh$_4$][Cu(η^5-4)]·2H$_2$O: space group $P2_1/n$ ($0k0$ absent for k odd, $h0l$ absent for $h + l$ odd); the unit cell parameter at room temperature [a = 9.263 (1) Å, b = 14.446 (3) Å, c = 26.792 (4) Å, β = 96.056 (13)°, V = 3564 (1) Å^3, Z = 4] were obtained by least-squares refinement of 25 2θ values. The data were collected on a crystal at room temperature with an Enraf-Nonius CAD4 diffractometer (graphite monochromator and Mo Kα radiation, λ = 0.7107 Å). The total in a hemisphere to $2\theta = 50°$, 14 252 ($+h,\pm k,\pm l$), yielded an average data set of 6248 reflections; 5182 had $I > 0$ and 2329 had $I > 3\sigma_I$. The three check reflections indicated an average linear decrease of 8.8% in intensity over the 266 h of data collection, and the intensity data were corrected accordingly and reduced to F^2. The coordinates of the Cu atom were derived from a Patterson map, and the remainder of the structure was revealed by Fourier maps. Hydrogen atoms were located from difference Fourier maps and introduced into the model with idealized positions and isotropic B = 4.0 A^2; they were not refined. Full-matrix least-squares refinement of atom coordinates and anisotropic U_{ij}'s for all non-hydrogen atoms minimizing $\sum w\Delta^2$ with weights $w = \sigma_{F^2}{}^{-2}$ and $\Delta = F_o{}^2 - (F_c{}^2/k)^2$ gave S (goodness-of-fit) $[\sum w\Delta^2/(n-p)]^{1/2} = 1.42$ (p = 433), $R_F = (\sum||F_o| - |F_c||/\sum|F_o|$ for $I > 0) = 0.144$, and $R_{3\sigma}$ (R for $I > 1\sigma_I$) = 0.061; average final shift/error > 0.10. Final atom coordinates are given in Table I. All calculations were carried out on a VAX 11/750 computer using the CRYRM system of programs. The form factors were taken from ref 21 and those for Cu and P were corrected for anomalous dispersion.

Electrochemical Data. Cyclic voltammetry was performed on a Princeton Applied Research Model 173/179 potentiostat/digital coulometer equipped with positive feedback *ir* compensation and a Model 175 universal programmer. Current voltage curves were recorded on a Houston Instruments Model 2000 X-Y recorder.

Acetonitrile (Mallinckrodt) and dichloromethane (EM Science) were distilled from calcium hydride on to activated 3-Å molecular sieves and stored under argon. Tetrabutylammonium hexafluorophosphate was recrystallized twice from acteone/ether and vacuum dried at 80 °C. Sodium perchlorate was recrystallized twice from absolute ethanol and vacuum dried at 100 °C. Supporting electrolyte concentration in all cases was 0.1 M, and copper concentrations were typically 0.5–3 mM. The working electrode was a glassy carbon disk (0.32 cm^2) which was polished with 0.3 μm polishing powder, sonicated, washed with distilled water and acetone, and vacuum dried. A silver wire quasi-reference electrode and platinum gauze counter electrode were used. At the conclusion of each experiment ferrocene was added as an internal potential standard. All formal potentials were taken as the average of anodic and cathodic peak potentials and are reported vs. the ferrocinium/ferrocene couple which was consistently measured as +0.39 V vs. SCE in acetonitrile and +0.48 V vs. SCE in methylene chloride. Peak-to-peak separation of the ferrocinium/ferrocene couple was similar to that of the copper couples in

---

[15] (a) Mock, W. L. Ph.D. Thesis, Harvard University, Cambridge, MA, 1964, 128–130. (b) Bushby, R. J.; Pollard, M. D. *J. Chem. Soc., Perkin Trans 1* **1979**, 2401–2408.

Table I. Atomic Coordinates and U_{eq}'s ($\times 10^4$)

atom	x	y	z	U_{eq}, Å^2
Cu	893.0 (8)	1864.4 (6)	756.4 (3)	607 (2)
O1A	−2546 (4)	3162 (3)	1062 (2)	817 (13)
O1B	3342 (5)	195 (3)	1601 (2)	855 (15)
O2A	128 (4)	2588 (3)	248 (1)	772 (13)
O2B	2432 (4)	1447 (3)	454 (1)	730 (13)
N1A	−577 (5)	2212 (3)	1112 (2)	524 (14)
N1B	1535 (5)	1183 (3)	1299 (2)	536 (14)
C1A	−1550 (6)	2821 (4)	868 (2)	559 (18)
C1B	2741 (7)	690 (4)	1273 (2)	578 (19)
C2A	−1196 (7)	3031 (4)	352 (2)	673 (20)
C2B	3322 (6)	824 (4)	764 (2)	618 (20)
C3A	−1014 (9)	4051 (5)	289 (3)	1321 (31)
C3B	3330 (8)	−62 (4)	488 (2)	971 (25)
C4A	−2403 (7)	2657 (5)	2 (2)	1035 (26)
C4B	4837 (7)	1235 (5)	839 (3)	1039 (26)
C5A	−501 (6)	1838 (4)	1591 (2)	565 (17)
C5B	683 (6)	1245 (4)	1704 (2)	535 (18)
C6A	−1450 (6)	1984 (5)	1944 (2)	698 (19)
C6B	882 (6)	807 (4)	2154 (2)	650 (20)
C7A	−1204 (8)	1541 (5)	2396 (2)	874 (25)
C7B	−76 (8)	958 (5)	2505 (2)	835 (25)
P	4111 (2)	2494 (1)	3113 (1)	475 (4)
C11	2528 (6)	2236 (4)	3419 (2)	463 (16)
C12	1583 (6)	2942 (4)	3505 (2)	590 (18)
C13	373 (6)	2734 (5)	3745 (2)	719 (22)
C14	142 (6)	1857 (6)	3904 (2)	772 (23)
C15	1081 (7)	1156 (4)	3828 (2)	650 (19)
C16	2279 (6)	1350 (4)	3580 (2)	571 (17)
C21	3653 (6)	2923 (3)	2494 (2)	418 (15)
C22	2283 (6)	3203 (4)	2318 (2)	514 (16)
C23	2004 (6)	3553 (4)	1850 (2)	633 (19)
C24	3069 (7)	3626 (4)	1530 (2)	653 (20)
C25	4441 (7)	3347 (4)	1699 (2)	646 (19)
C26	4731 (6)	2990 (4)	2178 (2)	591 (18)
C31	5153 (6)	3338 (4)	3485 (2)	459 (16)
C32	5106 (7)	3382 (5)	3993 (2)	812 (22)
C33	5928 (8)	3999 (5)	4282 (2)	980 (28)
C34	6815 (7)	4586 (4)	4065 (2)	723 (21)
C35	6888 (6)	4558 (4)	3572 (2)	686 (20)
C36	6073 (6)	3942 (4)	3274 (2)	597 (18)
C41	5159 (6)	1458 (4)	3074 (2)	478 (17)
C42	6154 (6)	1198 (4)	3473 (2)	625 (19)
C43	6882 (6)	372 (5)	3447 (3)	749 (23)
C44	6609 (7)	−179 (4)	3031 (3)	806 (27)
C45	5638 (7)	78 (4)	2637 (2)	678 (20)
C46	4903 (6)	897 (4)	2660 (2)	539 (18)
O3	2661 (6)	3080 (4)	−157 (2)	1644 (22)
O4	−5267 (8)	4329 (4)	412 (3)	2099 (29)

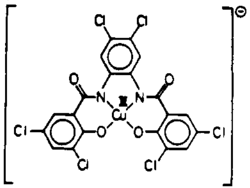
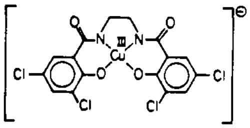
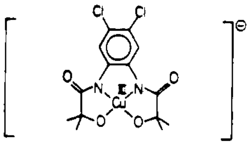
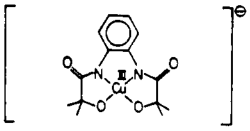
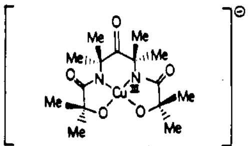
all cases. Plots of peak current vs. the square root of scan rate over the range 20–500 mV s^{-1} were made and found to be linear for couples that are stated to be reversible. All experiments were performed in standard two- or three-compartment electrochemical cells under an inert atmosphere.

Results and Discussion

Synthesis and Characterization of Complexes. The copper complexes listed in Table II were synthesized as salts of a variety of noncoordinating cations in either the +III or +II oxidation states depending on ease of handling. The choice of noncoordinating cations is important. Coordinating cations such as the sodium ion can significantly shift the formal potentials of the copper couples. For instance, the formal potential of the Cu(III/II) couple of $[Me_4N]_2[Cu(\eta^4\text{-}3)]$ is shifted by 210 mV to a more positive potential upon addition of 1.3 equiv of sodium perchlorate. The complexation of the sodium ion by the $[Cu(\eta^4\text{-}3)]$ anions is implicated, perhaps of a nature similar to that in $Na[Co(\eta^4\text{-}4)]\cdot((CH_3)_2CO)$ where the complex ion acts as a bidentate ligand bonding to the sodium ion through each alkoxide oxygen.[13]

An X-ray crystal structure determination for $[PPh_4][Cu(\eta^4\text{-}4)]\cdot 2H_2O$ reveals a square-planar environment for the metal center with normal bond distances and angles for the copper(III) formulation (see Figure 1 and Table I).[11-14] The Cu–N$_{amido}$ bond distances (1.813 (4) and 1,804 (4) Å are very similar to those found for the copper(III) tripeptide complex of tri-α-aminoisobutyric acid (1.801 (4) and 1.804 (5) Å).[4]

Table II. Copper(III/II) Couple Formal Potentials (V vs. Fc$^+$/Fc)

 $[Cu(\eta^4\text{-}1)]^-$	0.025	0.140	110 (20)
 $[Cu(\eta^4\text{-}2)]^-$	-0.140	-0.100	45 (45)
 $[Cu(\eta^4\text{-}3)]^-$	-0.920	-0.848	70 (20)
 $[Cu(\eta^4\text{-}4)]^-$	-0.945	-0.835	110 (20)
 $[Cu(\eta^4\text{-}5)]^-$	-1.080	-1.000	80 (10)

[a] $[(n\text{-}C_4H_9)_4N]^+$ salt employed. [b] $[(CH_3)_4N]^+$ salt employed. [c] $[PPh_4]^+$ salt employed. [d] Difference in formal potentials of copper(III/II) couples after difference for reference couple (90 mV) subtracted away.

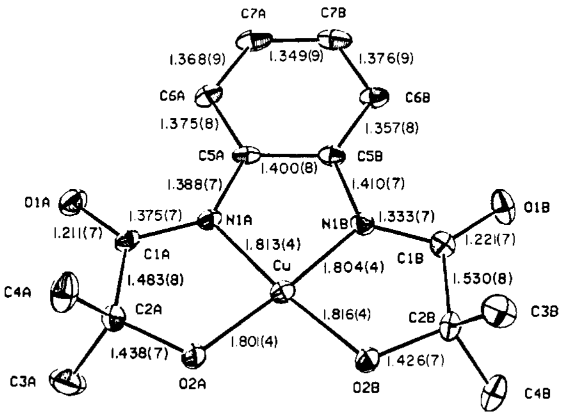


Figure 1. Structure of the ion $[Cu(\eta^4\text{-}4)]^-$ in $[PPh_4][Cu(\eta^4\text{-}4)]\cdot 2H_2O$.

Formal Oxidation State Assignments for Copper Complexes. The formal oxidation state assignment to the metal center of an inorganic complex is a useful communication device in inorganic chemistry.[16] As copper(III) is a rare oxidation state, it is appropriate to ask if the oxidized PAC ligand species are correctly formulated as copper(III) complexes. The formal oxidation state is assigned as the residual charge on the isolated metal center that

---

(16) For recent discussions of the oxidation state formalism see: (a) Holleran, E. M.; Jespersen, N. D. *J. Chem. Educ.* **1981**, *58*, 670. (b) Sisler, H. H.; Van der Werf, C. A. *J. Chem. Educ.* **1980**, *57*, 42–44. (c) Summerville, D. A.; Jones, R. D.; Hoffman, B. M.; Basolo, F. *J. Chem. Educ.* **1979**, *56*, 157–162. (d) Herron, J. D. *J. Chem. Educ.* **1975**, *52*, 602–603, 51–52. (e) Reference 17c.

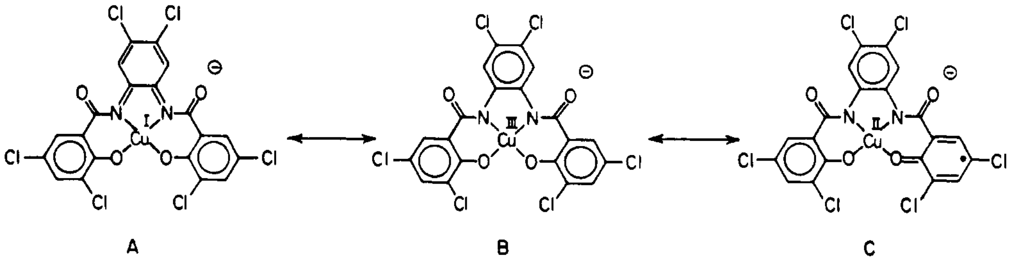


Figure 2. Different electronic forms of the complex ion $[Cu(\eta^4\text{-}\mathbf{1})]^-$ in which the formal oxidation states of the metal centers are different.

results when all the ligands are conceptually removed in their closed valence shell configurations. Ambiguity in formal oxidation state assignments can arise when a metal center is complexed to an unsaturated ligand with an extended π system that is mixed with the metal orbitals. Often the structure of such a complex is best described by mixing electronic descriptions that represent the extreme cases of metal-localized and ligand-localized redox processes. The formal oxidation state of the metal center is different in each case. Ligands of this type are called *noninnocent*.[17] In addition to the noninnocent character of certain unsaturated ligands, ligand-localized oxidations can occur in principal for all ligands and are more probable for ligands with lower ionization energies.

In Figure 2 several forms of the complex $[Cu(\eta^4\text{-}\mathbf{1})]^-$ are depicted in which the formal oxidation states of the metal centers are different. In principal, $[\eta^4\text{-}\mathbf{1}]^{4-}$, $[\eta^4\text{-}\mathbf{2}]^{4-}$, $[\eta^4\text{-}\mathbf{3}]^{4-}$, and $[\eta^4\text{-}\mathbf{4}]^{4-}$ can be noninnocent. There is more than one reasonable closed-shell form in which each ligand can be conceptually removed from the metal, A and B. Furthermore, several radical species could be involved, e.g., C. Are the oxidized species of these ligands best described as copper(III) complexes?

The complex $[Cu(\eta^4\text{-}\mathbf{5})]^-$ contains no easily oxidized or noninnocent ligand groups and thus serves as a copper(III) benchmark for these systems. The remarkably low copper(III/II) couple of -1.08 (vs. Fc^+/Fc, -0.60 vs. SCE) is evidence of the powerful donor capacity of the $[\eta^4\text{-}\mathbf{5}]^-$ PAC ligand and is also evidence against any ligand-centered character to this oxidation.

Do solvent effects play a role in the shifts in formal potentials that occur with ligand substitutions (Table II)? The differences between the formal potentials in acetonitrile are similar to those in dichloromethane which is generally regarded as a noncoordinating solvent.[18] When a correction is made for the different formal potentials of the Fc^+/Fc reference couple in the two media (0.480 V vs. SCE in CH_2Cl_2, 0.390 V vs. SCE in CH_3CN), the changes lie within 10–20 mV with one exception: the $[Cu(\eta^4\text{-}\mathbf{2})]^{-/2-}$ couple where the change is 40 mV. These small differences suggest that there is no strong coordination of acetonitrile to the copper(II) species. It has been reported that water coordination to copper(II) polypeptide complexes influences the formal potentials of the copper(III/II) couples measured in aqueous media.[4]

The trend in formal potentials as the aromatic groups are systematically replaced by aliphatic groups suggests that the degree of noninnocence is small, i.e., that all the oxidized species are best described as copper(III) complexes. If oxidation of $[Cu(\eta^4\text{-}\mathbf{1})]^{2-}$ (Table II) occurs principally from a π bond of the dichlorophenylene unit, then replacement of this group by the ethylene unit of $[Cu(\eta^4\text{-}\mathbf{2})]^{2-}$ should result in an increased formal potential. The formal potential is observed to decrease by 165 mV in CH_2Cl_2. Some decrease is to be expected for a metal-centered oxidation perturbed by the stronger inductive donor capacity of the ethylene relative to the dichlorophenylene fragment. Similarly, removal of two of the chlorine substituents of $[Cu(\eta^4\text{-}\mathbf{3})]^{2-}$ to give $[Cu(\eta^4\text{-}\mathbf{4})]^{2-}$ results in a small negative shift in the formal potential (-25-mV shift to -0.945 V in CH_2Cl_2). Increased inductive donation to the metal center is the probable reason for this change as it is most unlikely that oxidation of $[Cu(\eta^4\text{-}\mathbf{4})]^{2-}$ could be ligand-centered to a significant degree at this very negative potential. The free ligand $H_4\mathbf{4}$ shows no tendency to oxidize below $+0.750$ V. If oxidation occurs significantly from the π orbitals of the dichlorophenoxide units of $[Cu(\eta^4\text{-}\mathbf{1})]^{2-}$, substitution of these groups by the alkoxide donors of $[Cu(\eta^4\text{-}\mathbf{3})]^{2-}$ might be expected to result in a positive shift in the formal potential. The formal potential drops dramatically by 0.945 V (CH_2Cl_2). This is consistent with increased covalent character in the metal–ligand σ bonds resulting from the substantially greater polarizability of the alkoxide relative to the phenoxide oxygen donors or, in other words, in an increased donor capacity of $[\eta^4\text{-}\mathbf{3}]^-$ relative to $[\eta^4\text{-}\mathbf{1}]^-$. Stronger metal–ligand σ bonding should destabilize the singly occupied σ^* HOMO of the copper(II) complex. Since $H_4\mathbf{1}$ shows no tendency to oxidize below 0.600 V, it is likely that oxidation of $[Cu(\eta^4\text{-}\mathbf{1})]^{2-}$ is primarily metal-centered.[19]

Conclusion

A new series of copper(III) complexes is described in this report. To our knowledge, those containing alkoxide donors exhibit the most negative copper(III/II) formal potentials yet reported for complexes with first-row donor complements. These results illustrate that the alkoxide-containing PAC ligands are very powerful donors when compared with other such ligand complements. This property is valuable for stabilizing unusual high oxidation states of the later transition metals. The formal potentials of the copper(III/II) couples listed in Table II vary by over 1.1 V, a substantial range considering that the PAC ligands in the series appear to be superficially similar. The large variation is a further reflection[2] of the acute sensitivity of copper(III/II) couples to the donor properties of ligand complements. The differences can be explained in terms of the changes in basicity of the ligand without invoking contributions from ligand-centered redox processes. While the separation of σ and π-donor effects is not possible on the basis of the current information, the experimental observations can be rationalized if is is assumed that the donor effects are transmitted to the copper center through molecular orbitals of σ symmetry. In terms of this rationalization, all the oxidized complexes are properly regarded as copper(III) species. The approach taken here of following the trend in the formal potentials in a series of related complexes while replacing potentially noninnocent ligand fragments for innocent ligand fragments is a valuable method for determining the most appropriate formal oxidation state assignment for the metal center.

It should be noted that in other metal systems the increase in donor capacity that accompanies the alkoxide for phenoxide substitution can have chemical consequences other than a lowering of the formal potentials of the various couples. Thus, octahedral cobalt(III) complexes of phenoxide-containing PAC ligands, e.g., $[Co(\eta^4\text{-}\mathbf{1})(t\text{-}Bupy)_2]^-$, are stable and can be reversibly oxidized

---

(17) For references concerning noninnocent ligands see: (a) Clarke, M. J. *Comments Inorg. Chem.* **1984**, *3*, 131–151. (b) Pierpont, C. G.; Buchanan, R. M. *Coord. Chem. Rev.* **1981**, *38*, 45–87. (c) Levason, W.; McAuliffe, C. A. *Coord. Chem. Rev.* **1974**, *12*, 151–184.

(18) Dichloromethane is almost always considered to be a noncoordinating solvent. For recent reports including formulations of dichloromethane adducts of platinum see: (a) Strukul, G.; Michelin, R. A. *J. Am. Chem. Soc.* **1985**, *107*, 7563–7569. (b) Strukul, G.; Michelin, R. A.; Orbell, J. D.; Randaccio, L. *Inorg. Chem.* **1983**, *22*, 3706–3713.

(19) We do not argue that the above electrochemical evidence definitely identifies a particular locus of oxidation in the oxidized species. It would not be impossible for each of the oxidations to be ligand centered and for the aliphatic substitutions to effect a large enough increase in inductive donation to produce the observed negative, instead of positive, shifts in formal potentials. However, since all of the free base ligands are oxidized at potentials more positive than the couples in question, we believe that all the oxidized species are best formulated as copper(III) complexes.

to stable octahedral cobalt(IV) species at mild potentials.[12] However, the alkoxide-containing PAC ligands produce stable square-planar cobalt(III) complexes which have little affinity for axial ligands.[13] The change also presumably results from an increase in the covalent character of the in-plane σ bonding which should raise the energy of metal orbitals with axial σ symmetry and weaken the cobalt–axial ligand bonding.[20] This understanding provides a potentially valuable method for producing vacant sites in highly oxidized metal complexes.

Acknowledgment. We acknowledge the Rohm and Haas Co., the Atlantic Richfield Corp. of America, and the National Science Foundation (Grants CHE-83-11579 to F.C.A. and CHE-84-06198 to T.J.C.) for support of this work. We acknowledge Professor Paul Engel of Rice University for helpful discussions.

Supplementary Material Available: Listing of bond distances and angles and Gaussian amplitudes (4 pages); a listing of structure factor amplitudes (31 pages). Ordering information is given on any current masthead page.

---

(20) For a recent article discussing the occurrence of square-planar cobalt(III) complexes see: Rao, Ch. P.; Dorfman, J. R.; Holm, R. H. *Inorg. Chem.* **1986**, *25*, 428–439.

(21) *International Tables* of *X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV, Table 2.2B.

Molecular Structures and Electron-Transfer Kinetics for Some Pentacoordinate Cu^I/Cu^{II} Redox-Active Pairs

John A. Goodwin,[†] David M. Stanbury,*[†] Lon J. Wilson,*[†] C. W. Eigenbrot,[‡] and W. Robert Scheidt*[‡]

Contribution from the Department of Chemistry, William Marsh Rice University, Houston, Texas 77251, and the Department of Chemistry, University of Notre Dame, Notre Dame, Indiana 46556. *Received August 11, 1986*

Abstract: Crystal structures of the copper(I) and copper(II) complexes of the pentadentate nitrogen-bonding ligand, {bis-2,6-[1-((2-pyridin-2-ylethyl)imino)ethyl]pyridine} (= $(py)_2DAP$), $[Cu^I(py)_2DAP]^+$ and $[Cu^{II}(py)_2DAP]^{2+}$, have been solved as the tetrafluoroborate salts. The copper(I) complex was obtained as the hemi-methylene chloride, water solvate; the copper(II) complex was obtained as unsolvated crystals. Crystal data for $[Cu^I(py)_2DAP]^+$ are as follows: $CuF_4N_5C_{23}BH_{25}\cdot{}^1/_2CH_2Cl_2\cdot{}^1/_2H_2O$, $a = 15.678$ (2) Å, $b = 8.807$ (1) Å, $c = 20.727$ (2) Å, $\beta = 110.69$ (1)°, $Z = 4$, monoclinic, space group $P2/C$. Crystal data for $[Cu^{II}(py)_2DAP]^{2+}$ are as follows: $CuF_8N_5C_{23}B_2H_{25}$, $a = 11.166$ (2) Å, $b = 12.992$ (3) Å, $c = 10.364$ (2) Å, $\alpha = 106.29$ (2)°, $\beta = 109.22$ (2)°, $\gamma = 89.97$ (2)°, $Z = 2$, triclinic, space group $P\bar{1}$. Both complexes are pentacoordinate about the copper center. The copper(I) complex has an idealized trigonal bipyramidal structure with average Cu^I–N bond distances of 2.07 Å (trigonal plane) and 2.26 Å (axial). The coordination geometry of the copper(II) species is less regular. The average Cu^{II}–N bond distance is 0.12 Å shorter than the average Cu^I–N distance, but some bond lengths change substantially more than others. The kinetics of the electron self exchange for this couple has been studied in CD_3CN by dynamic NMR methods to yield a rate constant of $k'_{11} = 1.71 \times 10^3$ M^{-1} s^{-1} at 25 °C and ionic strength = 50 mM (Me_4NBF_4). The kinetics of electron cross exchange in CH_3CN has also been investigated by reducing **1**, $[Cu^{II}(py)_2DAP]^{2+}$, with two similar complexes, **2**, $[Cu^I(imidH)_2DAP]^+$, and **3**, $[Cu^I(imidR)_2DAP]^+$, and monitoring the reactions with stopped-flow techniques. The apparent rate constants at 25 °C and $\mu = 50$ mM (n-Bu_4NBF_4) are $k'_{12} = 6.44 \times 10^4$ M^{-1} s^{-1} and $k'_{13} = 6.10 \times 10^4$ M^{-1} s^{-1}. Stopped-flow studies of the ionic strength dependence indicate that ion pair formation between the copper(II) species and BF_4^- inhibits electron transfer. Under the assumption of an outer-sphere mechanism, Marcus cross relation calculations have been carried out to estimate the self-exchange rate constants for **2** and **3**. With correction of the kinetics and thermodynamics data for medium effects, these calculations have yielded $k^\circ_{22} = 1.64 \times 10^3$ M^{-1} s^{-1} and $k^\circ_{33} = 3.33 \times 10^3$ M^{-1} s^{-1} at $\mu = 0$ M, which may be compared with a value of $k^\circ_{11} = 3.05 \times 10^2$ M^{-1} s^{-1}. These electron exchange results apparently are the first to be reported for a Cu(I)/Cu(II) couple in which the coordination number is the same in the two oxidation states.

Cuproproteins involving biological redox chemistry have recently stimulated interest in deciphering relationships between the structural and electron-transfer properties of Cu(II)/Cu(I) couples at active sites.[1] Foremost among these are the blue copper proteins where X-ray crystallography has revealed active site structures with nitrogen, sulfur, and possibly oxygen donor atoms arranged around copper in tri-, tetra-, and possibly pentacoordinate geometries. In particular, plastocyanin[2] and azurin[3] have been well-studied and their relatively large self-exchange rates ($k'_{11} = 10^4$–10^6 M^{-1} s^{-1})[4,5] have been attributed to small coordination-sphere reorganization around copper during the outer-sphere Cu(II) ⇄ Cu(I) electron-transfer processes.[6]

One approach toward further understanding these biological electron-transfer processes is to study small molecule copper compounds of related structure and/or function. For the blue copper proteins, this "model compound" approach has been taken by others,[7] but complicating factors such as copper–ligand bond

---

[†] William Marsh Rice University.

[‡] University of Notre Dame.

(1) (a) *Copper Proteins*; Spiro, T. G., Ed.; Wiley: New York, **1981**. (b) *Biochemical and Inorganic Aspects of Copper Coordination Chemistry*; Karlin, K. D., Zubieta, J., Eds.; Adenine Press: **1985**. (c) *Copper Proteins and Copper Enzymes*; Lontie, R., Ed.; CRC: Boca Raton, FL, **1984**; Vols. I–III.

(2) Freeman, H. C. In *Coordination Chemistry—21*; Laurent, J. P., Ed.; Pergamon: New York, 1981; p 29–51.

(3) Norris, G. E.; Anderson, B. F.; Baker, E. N. *J. Am. Chem. Soc.* **1986**, *108*, 2784–2785.

(4) Armstrong, F. A.; Driscoll, P. C.; Hill, H. A. O. *FEBS Lett.* **1985**, *190*, 242–248.

(5) (a) Ugurbil, K.; Mitra, S. *Proc. Natl. Acad. Sci. U.S.A.* **1985**, *82*, 2039–2043. (b) Groeneveld, C. M.; Canters, G. W. *Eur. J. Biochem.* **1985**, *153*, 559–564.

(6) Gray, H. B.; Malmstrom, B. G. *Comments Inorg. Chem.* **1983**, *2*, 203–209.

0002-7863/87/1509-2979$01.50/0