ordinated phosphorus atoms in a structure involving bridging bidentate dppm ligands.

Experimental Section

NMR spectra were recorded on a multinuclear Bruker WP-80 spectrometer operating in the FT mode. Chemical shifts are given in ppm relative to the high frequency of 85% H_3PO_4 or aqueous $Hg(ClO_4)_2$ (2 mmol of HgO/cm^3 of 60% $HClO_4$); coupling constants are in hertz. Elemental analyses were obtained on a Heraeus EA 415 apparatus.

Literature methods were used to prepare $[Hg(Me_2SO)_6](O_3SCF_3)_2$,[9] $[Pt(\eta^2\text{-dppm})_2]Cl_2$, and $[Pt(\eta^2\text{-dppe})_2]Cl_2$.[10]

Preparation of $[Hg(\eta^1\text{-dppm})_2](O_3SCF_3)_2$. $[Hg(Me_2SO)_6](O_3SCF_3)_2$ (96.7 mg, 0.1 mmol) and dppm (96 mg, 0.2 mmol) were mixed together in a Schlenk tube under dinitrogen in 1 cm^3 of CH_2Cl_2, and the mixture was stirred at room temperature for 15 min. The CH_2Cl_2 was evaporated, and the product was precipitated from the oily residue as a colorless microcrystalline powder by adding 1 cm^3 of H_2O. The precipitate was filtered, washed with 1 cm^3 of H_2O, and vacuum-dried, giving an almost quantitative yield; mp 105 °C.[11]

Preparation of $[Hg(\eta^2\text{-dppe})_2](O_3SCF_3)_2$ by the above method gave the product, recrystallized from toluene/ethanol/petroleum ether as colorless crystals. The yield was about 80%; mp 227 °C.[11]

Acknowledgment. Thanks are due to the Fonds zur Förderung der Wissenschaft, Vienna, for making available the NMR spectrometer.

Registry No. $[HgL_2](O_3SCF_3)_2$ (L = dppm), 93503-32-3; $[HgL_2](O_3SCF_3)_2$ (L = dppe), 93503-34-5; $[Hg(Me_2SO)_6](O_3SCF_3)_2$, 76703-09-8.

---

(9) Peringer, P. *J. Inorg. Nucl. Chem.* **1980**, *42*, 1501.

(10) Brown, M. P.; Fisher, J. R.; Manojlovic-Muir, L.; Muir, K. W.; Puddephatt, R. J.; Thomson, M. A.; Seddon, K. R. *J. Chem. Soc., Chem. Commun.* **1979**, 931. Westland, A. D. *J. Chem. Soc.* **1965**, 3060.

(11) Satisfactory elemental analyses were obtained.

Contribution No. 3512 from the Central Research
and Development Department, E. I. du Pont
de Nemours and Company, Experimental Station,
Wilmington, Delaware 19898

Copper(I) Complexes with Unsaturated Small Molecules. Synthesis and Properties of Monoolefin and Carbonyl Complexes

Jeffery S. Thompson* and Rose M. Swiatek

Received June 12, 1984

In this contribution, we present the synthesis and properties of monoolefin and carbonyl complexes that establish the similarities and differences in the copper(I) coordination chemistry with these small molecules. Our recently reported study of Cu(I)–di-2-pyridylamine complexes with monoolefins, acetylene, and carbon monoxide demonstrates some of the features of cuprous complexes with these small molecules.[1,2] In particular, this study suggests that the structural chemistry is comparable to that of Ni(0) and other d^{10} metals.[5,6] Monoolefin complexes generally have trigonal-planar geometries, but tetrahedral complexes can be prepared with the proper choice of ligands.[1-4] Carbonyl complexes tend toward four-coordinate geometries,[6,7] although higher coordination numbers are also known.[8] However, our studies also show that some significant differences exist in the coordination chemistry of the two types of d^{10} metal ions. Olefin and acetylene bonds are not significantly lengthened on coordination to Cu(I) ions, unlike the significant increases in bond lengths of these molecules on coordination to Ni(0) ions.[5,6] This lack of effect on coordination may be a manifestation of the poor π-back-bonding ability of the cuprous ion. Similarly, cuprous ion does not appear to coordinate more than one carbonyl group, whereas Ni(0) complexes with two, three, and four carbonyl groups are well-known.[6] Other species, including counterions such as perchlorate and tetraphenylborate, occupy the fourth site.[1,9]

The complexes described here were prepared to determine whether the properties suggested in our previous studies[1-4] are general features of copper coordination chemistry with these molecules. A series of nitrogen-donating ligands is used to prepare ethylene, propylene, cyclohexene, and carbonyl complexes. The type of coordinated nitrogen atom varies from tertiary amines to aromatic heterocyclic nitrogen donors. Our Cu(I)–monoolefin complexes reported here and elsewhere[1-3] are the only ones that are both *stable* to loss of olefin and *soluble* in common solvents and can thus be spectrally characterized. We assign structures to these complexes on the basis of the similarities of their spectral parameters to those of complexes of known structure.

Experimental Section

General Methods. All chemicals were reagent grade and were used as received unless otherwise noted. The solvents methanol, diethyl ether, and cyclohexene were deaerated with prepurified nitrogen and stored over molecular sieves (4A), which were activated prior to use by heating at approximately 250 °C under high vacuum and then stored under nitrogen. *N,N,N',N'*-Tetramethylethylenediamine (TMEN) and *N,N,N',-N'*-tetraethylethylenediamine (TEEN) were thoroughly degassed and then stored over activated molecular sieves under nitrogen. Standard glovebox and Schlenkware techniques were used to handle air-sensitive compounds. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, TN, and by Schwarzkopf Microanalytical Laboratory, Woodside, NY. Infrared spectra were obtained as Nujol mulls with a Perkin-Elmer 283-B infrared spectrophotometer. NMR spectra were obtained in deuterioacetone with a Perkin-Elmer EM-390 spectrometer; all reported peak positions are relative to external tetramethylsilane.

General Methods for Preparation of Copper(I) Complexes. Copper perchlorate hexahydrate (0.25 g, 0.67 mmol) and copper dust (0.20 g, 3.1 mmol) were stirred in 10 mL of methanol overnight under an atmosphere of the appropriate gas (ethylene, propylene, or carbon monoxide). *Caution! The Cu(I) complexes produced in this step are unstable and can explode if taken to dryness.*[10] The ligand (0.16 g of TMEN, 0.23 g of TEEN, 0.21 g of 2,2'-bipyridine, or 0.24 g of 1,10-phenanthroline, 1.3 mmol) was then added, TMEN and TEEN as methanol solutions and 2,2'-bipyridine (bpy) and 1,10-phenanthroline (OP) as powders. After complete addition, the reaction mixture was stirred for approximately 0.5 h and then filtered under nitrogen pressure. The volume of the filtrate was reduced with a stream of the appropriate gas. White, slightly yellow, or gray microcrystalline products were obtained by adding diethyl ether and collected by filtration under nitrogen.

The above procedure with the following changes was used to prepare the cyclohexene complexes: use of an initial reaction mixture of 5 mL of methanol and 5 mL of cyclohexene and elimination of the concentration step. In addition to the ligands indicated above, the ligand di-2-pyridylamine ($NH(py)_2$) (0.23 g, 1.3 mmol) was also used.

(Ethylene)(tetramethylethylenediamine)copper(I) Perchlorate (1). Anal. Calcd for $C_8H_{20}ClCuN_2O_4$: C, 31.27; H, 6.56; N, 9.12. Found:

---

(1) Thompson, J. S.; Whitney, J. F. *Inorg. Chem.* **1984**, *23*, 2813–2819.

(2) Thompson, J. S.; Whitney, J. F. *J. Am. Chem. Soc.* **1983**, *105*, 5488–5490.

(3) Thompson, J. S.; Harlow, R. L.; Whitney, J. F. *J. Am. Chem. Soc.* **1983**, *105*, 3522–3527.

(4) Thompson, J. S.; Whitney, J. F. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1984**, *C40*, 756–759.

(5) (a) Ittel, S. D.; Ibers, J. A. *Adv. Organomet. Chem.* **1976**, *14*, 33–61. (b) Mingos, D. M. P. In "Comprehensive Organometallic Chemistry"; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds; Pergamon Press: New York, 1982; Vol. 3, pp 1–88. (c) Jolly, P. W. *Ibid.*, Vol. 6, pp 101–143. (d) Hartley, F. R. *Ibid.*, Vol. 6, pp 471–762.

(6) Jolly, P. W.; Wilke, G. "The Organic Chemistry of Nickel"; Academic Press: New York, 1974; Vol. I, pp 1–93.

(7) (a) Sorrell, T. N.; Jameson, D. L. *J. Am. Chem. Soc.* **1983**, *105*, 6013–6018. (b) Sorrell, T. N.; Malachowski, M. R. *Inorg. Chem.* **1983**, *22*, 1883–1887.

(8) McCool, M. W.; Marsh, R. E.; Ingle, D. M.; Gagne, R. R. *Acta Crystallogr., Sect. B* **1981**, *B37*, 935–937.

(9) Pasquali, M.; Floriani, C.; Gaetani-Manfredotti, A. *Inorg. Chem.* **1980**, *19*, 1191–1197.

(10) Ogura, T. *Inorg. Chem.* **1976**, *15*, 2301–2303.

0020-1669/85/1324-0110$01.50/0

C, 31.29; H, 6.70; N, 8.87. IR (cm^{-1}): 1525 m, 1425 m, 1380 s, 1370 m, 1360 w, 1295 s, 1255 s, 1205 w, 1170 w, 1130 s, 1085 s, 1045 m, 1020 s, 1005 w, 950 s, 835 w, 805 s, 770 m, 720 w, 620 s. ^{1}H NMR (ppm): 4.31 (s, 4 H), 2.92 (s, 4 H), 2.74 (s, 12 H).

(Propylene)(tetramethylethylenediamine)copper(I) Perchlorate (2). Anal. Calcd for $C_9H_{22}ClCuN_2O_4$: C, 33.65; H, 6.90; N, 8.72. Found: C, 31.01; H, 6.44; N, 8.66. IR (cm^{-1}): 1530 w, 1420 w, 1290 m, 1245 m, 1200 w, 1165 w, 1130 m, 1085 s, 1045 m, 1025 m, 1005 w, 950 m, 930 w, 890 w, 800 s, 775 m, 720 m, 620 s. ^{1}H NMR (ppm): 5.17 (multiplet, 1 H), 4.27 (t, 2 H), 2.90 (s, 4 H), 2.75 (s, 12 H), 1.75 (d, 3 H).

(Cyclohexene)(tetramethylethylenediamine)copper(I) Perchlorate (3). Anal. Calcd for $C_{12}H_{26}ClCuN_2O_4$: C, 39.89; H, 7.25; N, 7.75. Found: C, 39.60; H, 7.14; N, 7.53. IR (cm^{-1}): 1525 w, 1420 w, 1365 w, 1355 w, 1340 w, 1290 m, 1245 m, 1205 w, 1195 w, 1170 w, 1150 w, 1130 w, 1085 s, 1045 m, 1025 m, 1005 w, 965 w, 950 m, 880 w, 870 w, 800 s, 765 m, 720 w, 620 s. ^{1}H NMR (ppm): 5.37 (s, 2 H), 2.93 (s, 4 H), 2.77 (s, 12 H), 2.1 (broad multiplet, 4 H), 1.67 (broad multiplet, 4 H).

(Perchlorato)carbonyl(tetramethylethylenediamine)copper(I) (4). Anal. Calcd for $C_7H_{16}ClCuN_2O_5$: C, 27.37; H, 5.25; N, 9.12. Found: C, 27.71; H, 5.73; N, 8.90. IR (cm^{-1}): 2110 s, 1415 w, 1295 w, 1250 m, 1200 w, 1110 s, 1055 s, 1010 w, 950 m, 930 m, 800 m, 770 w, 725 w, 620 m. ^{1}H (ppm): 2.80 (s, 4 H), 2.73 (s, 12 H).

(Ethylene)(tetraethylethylenediamine)copper(I) Perchlorate (5). Anal. Calcd for $C_{12}H_{28}ClCuN_2O_4$: C, 39.67; H, 7.77; N, 7.71. Found: C, 39.75; H, 8.13; N, 7.72. IR (cm^{-1}): 1525 m, 1355 w, 1340 w, 1315 w, 1305 w, 1265 m, 1180 m, 1160 m, 1145 s, 1085 s, 1020 m, 955 w, 915 w, 815 w, 800 w, 765 s, 730 m. ^{1}H NMR (ppm): 4.43 (s, 4 H), 3.01 (multiplet, 12 H), 1.25 (t, 12 H).

(Propylene)(tetraethylethylenediamine)copper(I) Perchlorate (6). Anal. Calcd for $C_{13}H_{30}ClCuN_2O_4$: C, 41.38; H, 8.01; N, 7.42. Found: C, 36.88; H, 7.33; N, 7.63. IR (cm^{-1}): 1535 w, 1315 w, 1265 w, 1180 w, 1155 w, 1140 w, 1085 s, 975 w, 935 w, 895 w, 850 w, 800 w, 765 m, 725 m. ^{1}H NMR (ppm): 5.30 (multiplet, 1 H), 4.36 (t, 2 H), 2.98 (multiplet, 12 H), 1.73 (d, 3 H), 1.23 (t, 12 H).

(Perchlorato)carbonyl(tetraethylethylenediamine)copper(I) (7). Anal. Calcd for $C_{11}H_{24}ClCuN_2O_5$: C, 36.36; H, 6.66; N, 7.71. Found: C, 36.24; H, 6.93; N, 7.75. IR (cm^{-1}): 2105 s, 2055 w, 1350 m, 1300 w, 1265 w, 1175 m, 1100 s, 1045 s, 915 m, 810 w, 790 w, 760 m, 730 m, 700 w. ^{1}H NMR (ppm): 2.95 (multiplet, 12 H), 1.15 (t, 12 H).

(Ethylene)(2,2′-bipyridine)copper(I) Perchlorate (8). Anal. Calcd for $C_{12}H_{12}ClCuN_2O_4$: C, 41.51; H, 3.48; N, 8.07. Found: C, 41.18; H, 3.37; N, 7.85. IR (cm^{-1}): 3120 w, 3080 w, 3060 w, 1605 m, 1600 s, 1575 w, 1565 w, 1525 m, 1495 s, 1425 w, 1320 m, 1295 w, 1260 m, 1225 w, 1200 w, 1180 m, 1160 m, 1085 s, 1045 w, 1030 m, 1020 w, 1010 w, 985 w, 965 w, 960 m, 930 w, 915 w, 815 w, 800 w, 775 s, 735 s, 660 w, 650 w. ^{1}H NMR (ppm): 8.99 (d, 2 H), 8.73 (d, 2 H), 8.43 (t, 2 H), 7.93 (t, 2 H), 4.92 (s, 4 H).

(Propylene)(2,2′-bipyridine)copper(I) Perchlorate (9). Anal. Calcd for $C_{13}H_{14}ClCuN_2O_4$: C, 43.22; H, 3.91; N, 7.75. Found: C, 42.94; H, 3.78; N, 7.55. IR (cm^{-1}): 3110 w, 3080 w, 1610 m, 1600 m, 1575 w, 1570 w, 1530 w, 1490 m, 1320 m, 1250 m, 1230 w, 1180 w, 1165 w, 1115 s, 1090 s, 1045 w, 1030 m, 1020 w, 1005 w, 995 w, 985 w, 945 w, 930 w, 915 w, 890 w, 815 w, 775 s, 740 s, 710 w, 665 w, 650 w, 640 w. ^{1}H NMR (ppm): 8.89 (d, 2 H), 8.77 (d, 2 H), 8.35 (t, 2 H), 7.87 (t, 2 H), 5.63 (multiplet, 1 H), 4.70 (t, 2 H), 1.85 (d, 3 H).

(Cyclohexene)(2,2′-bipyridine)copper(I) Perchlorate (10). Anal. Calcd for $C_{16}H_{18}ClCuN_2O_4$: C, 47.88; H, 4.52; N, 6.98. Found: C, 47.51; H, 4.53; N, 6.89. IR (cm^{-1}): 3080 w, 1610 m, 1600 m, 1575 w, 1565 w, 1522 w, 1490 m, 1350 w, 1320 w, 1315 w, 1260 w, 1250 m, 1240 w, 1220 w, 1210 m, 1175 m, 1160 m, 1150 m, 1100 s, 1085 s, 1045 w, 1035 w, 1025 m, 1015 w, 1010 w, 980 w, 960 m, 925 w, 895 m, 870 w, 810 w, 760 s, 730 m, 720 w, 675 w, 660 w, 650 w, 635 w. ^{1}H NMR (ppm): 8.93 (d, 2 H), 8.70 (d, 2 H), 8.40 (t, 2 H), 7.90 (t, 2 H), 5.63 (s, 2 H), 2.1, 1.65 (multiplet, 4 H).

(Perchlorato)carbonyl(2,2′-bipyridine)copper(I) (11). Anal. Calcd for $C_{11}H_8ClCuN_2O_5$: C, 38.05; H, 2.32; N, 8.07. Found: C, 38.24; H, 2.24; N, 8.03. IR (cm^{-1}): 2110 s, 2060 w, 1605 m, 1600 m, 1575 w, 1570 w, 1490 w, 1325 m, 1250 m, 1225 w, 1180 m, 1160 m, 1110 s, 1055 s, 1040 s, 1025 s, 1015 m, 975 m, 925 m, 910 m, 895 w, 815 w, 770 s, 740 s, 660 w, 650 w. ^{1}H NMR (ppm): 9.09 (d, 2 H), 8.67 (d, 2 H), 8.37 (t, 2 H), 7.99 (t, 2 H).

(Ethylene)(1,10-phenanthroline)copper(I) Perchlorate (12). Anal. Calcd for $C_{14}H_{12}ClCuN_2O_4$: C, 45.29; H, 3.26; N, 7.54. Found: C, 44.92; H, 3.17; N, 7.47. IR (cm^{-1}): 3120 w, 3065 w, 1625 m, 1605 m, 1585 m, 1525 w, 1518 s, 1345 w, 1265 s, 1225 m, 1155 m, 1080 s, 1005 w, 988 w, 960 w, 905 m, 875 m, 860 s, 805 w, 785 m, 735 m, 725 s, 645 w. ^{1}H NMR (ppm): 9.33 (d, 2 H), 8.99 (d, 2 H), 8.37 (multiplet, 4 H), 5.00 (s, 4 H).

(Propylene)(1,10-phenanthroline)copper(I) Perchlorate (13). Anal. Calcd for $C_{15}H_{14}ClCuN_2O_4$: C, 46.76; H, 3.66; N, 7.27. Found: C, 46.52; H, 3.66; N, 7.16. IR (cm^{-1}): 3070 w, 1665 m, 1625 m, 1605 w, 1585 m, 1575 w, 1530 w, 1525 m, 1520 m, 1495 w, 1430 s, 1365 w, 1350 w, 1255 w, 1225 w, 1215 w, 1145 m, 1085 s, 1040 m, 1030 w, 1010 w, 1000 w, 990 m, 945 w, 930 m, 890 w, 870 m, 855 s, 830 w, 820 w, 780 m, 740 w, 725 s, 720 w, 650 w, 645 w, 625 s. ^{1}H NMR (ppm): 9.36 (d, 2 H), 8.99 (d, 2 H), 8.32 (multiplet, 4 H), 5.68 (multiplet, 1 H), 4.88 (t, 2 H), 1.88 (d, 2 H).

(Cyclohexene)(1,10-phenanthroline)copper(I) Perchlorate (14). Anal. Calcd for $C_{18}H_{18}ClCuN_2O_4$: C, 50.83; H, 4.26; N, 6.58. Found: C, 50.61; H, 4.22; N, 6.55. IR (cm^{-1}): 1625 w, 1605 w, 1585 w, 1515 m, 1305 w, 1260 w, 1225 w, 1210 w, 1145 m, 1085 s, 1010 w, 970 w, 960 w, 880 w, 870 m, 855 s, 815 w, 775 m, 725 s. ^{1}H NMR (ppm): 9.33 (d, 2 H), 8.98 (d, 2 H), 8.32 (multiplet, 4 H), 5.72 (s, 2 H), 2.1 (multiplet, 4 H), 1.65 (multiplet, 4 H).

(Perchlorato)carbonyl(1,10-phenanthroline)copper(I) (15). Anal. Calcd for $C_{13}H_8ClCuN_2O_5$: C, 42.06; H, 2.17; N, 7.55. Found: C, 41.75; H, 2.16; N, 7.60. IR (cm^{-1}): 3070 w, 2115 s, 2065 w, 1685 w, 1665 m, 1625 m, 1605 w, 1590 w, 1585 m, 1520 w, 1515 w, 1495 m, 1345 w, 1260 w, 1245 w, 1220 w, 1195 w, 1145 s, 1085 s, 1005 s, 980 w, 975 w, 930 w, 920 m, 905 w, 875 w, 870 w, 850 s, 820 w, 810 w, 785 w, 770 m, 740 w, 730 s, 725 w, 650 w, 645 w. ^{1}H NMR (ppm): 9.52 (d, 2 H), 8.93 (d, 2 H), 8.30 (q, 4 H).

(Cyclohexene)(di-2-pyridylamine)copper(I) Perchlorate (16). Anal. Calcd for $C_{16}H_{19}ClCuN_3O_4$: C, 46.16; H, 4.60; N, 10.09. Found: C, 45.91; H, 4.58; N, 9.94. IR (cm^{-1}): 3450 w, 3350 m, 3255 w, 3225 w, 3155 w, 3120 w, 1638 s, 1618 w, 1595 w, 1585 s, 1530 m, 1500 w, 1420 m, 1275 w, 1235 m, 1210 w, 1175 w, 1165 m, 1150 w, 1100 s, 1075 s, 1065 s, 1035 w, 1010 m, 995 w, 965 w, 950 w, 930 w, 910 w, 888 w, 872 w, 858 w, 835 w, 780 w, 765 s, 720 w, 610 m. ^{1}H NMR (ppm): 9.78 (s, 1 H), 8.32 (d, 2 H), 7.98 (multiplet, 2 H), 7.24 (multiplet, 4 H), 5.61 (s, 2 H), 2.20 (multiplet, 4 H), 1.60 (multiplet, 4 H).

Results

Synthesis and Properties. The syntheses of the Cu(I) complexes reported here are straightforward and are presented in eq 1 and 2. These preparations take advantage of the well-established

$$\mathrm{Cu(ClO_4)_2{\cdot}6H_2O + Cu^0 + X \xrightarrow{MeOH} \xrightarrow{L} [CuL(X)]ClO_4} \quad (1)$$

$$\mathrm{X = C_2H_4, C_3H_6;\ L = TMEN, TEEN, OP, bpy}$$

$$\mathrm{X = C_6H_{10};\ L = TMEN, NH(py)_2, OP, bpy}$$

$$\mathrm{Cu(ClO_4)_2{\cdot}6H_2O + Cu^0 + CO \xrightarrow{MeOH} \xrightarrow{L} [CuL(CO)ClO_4]} \quad (2)$$

$$\mathrm{L = TMEN, TEEN, OP, bpy}$$

reduction of Cu(II) salts by copper metal in the presence of small molecules such as ethylene and carbon monoxide.[1,10,11] The initial product in each case is presumably a Cu(I) adduct of the small molecule, but it was not isolated because of *the reported tendency of such adducts to explode when dry*;[10] rather, the ligand L was added slowly as a methanol solution (TMEN, TEEN) or a powder (NH(py)$_2$, bpy, OP). The preparations for the monoolefin complexes are also very general. The perchlorate complexes were prepared in this study because of the ease of crystallization; however, tetrafluoroborate and trifluoromethanesulfonate complexes were also prepared. These procedures are also suitable for a variety of ligands; however, as noted elsewhere, not all ligands tried yielded stable complexes.[1]

The synthetic procedures yield white, slightly yellow, or gray crystalline solids that give excellent analytical results for the indicated formulations, except for compounds **2** and **6**. The instability of these complexes as well as our lack of success in preparing a cyclohexene–TEEN complex probably results from steric interactions between the ligands in the copper coordination

---

(11) Hathaway, B. J.; Holah, D. G.; Postlethwaite, J. D. *J. Chem. Soc.* **1961**, 3215–3218.

Table I. Infrared (cm^{-1}) and ^1H NMR (ppm) Data for Coordinated Small Molecules with Bidentate Nitrogen Ligands[a]

	C_2H_4	C_3H_6	C_6H_{10}	CO
		TMEN		
IR	1525	1530	1525	2110
^1H NMR	4.31	5.17, 4.27	5.37	
		TEEN		
IR	1525	1535		2105
^1H NMR	4.43	5.30, 4.36		
		$NH(py)_2$		
IR	1505[b]	1515[b]	1530	2110[b]
^1H NMR	4.70[b]	5.48, 4.50[b]	5.61	
		bpy		
IR	1525	1530	1522	2110
^1H NMR	4.92	5.63, 4.70	5.63	
		OP		
IR	1525	1530	1515	2115
^1H NMR	5.00	5.68, 4.88	5.72	

[a] Olefin stretching frequencies and olefinic proton resonances are given. [b] Values from ref 1.

sphere. The destabilizing effect of other ligands on olefin coordination is a well-established property of transition-metal–olefin chemistry.[12] With all of the compounds reported here, no steps were taken to maintain an atmosphere of the appropriate gas over the sample; all compounds were handled and stored under nitrogen. All compounds are sensitive to the ambient atmosphere. These properties are identical with those of the Cu(I)–olefin complexes previously reported by us.[1-3]

Spectroscopic Data. The proton NMR data for all complexes (**1**–**16**) are consistent with the indicated formulations. All compounds, including those that gave poor elemental analyses, dissolve in solvents free of olefin or carbon monoxide without decomposition to yield clean NMR spectra. The positions of the olefin resonances (Table I) compare to those previously reported for the Cu(I) complexes with the ligands hydrotris(1-pyrazolyl)borate and hydrotris(3,5-dimethyl-1-pyrazolyl)borate[3] and appear to shift downfield along the series TMEN, TEEN, $NH(py)_2$, bpy, and OP. The data are consistent with formation of trigonal-planar Cu(I)–olefin complexes for all monoolefins. This structure has been confirmed by X-ray diffraction techniques for the $NH(py)_2$ complexes.[1,2,13]

The infrared data for these olefin complexes are consistent with the suggested formulations and support the assignment of a trigonal-planar geometry in each case. The perchlorate band appears as a single, sharp, strong band, indicating an ionic perchlorate group.[14] Although it is difficult to assign olefinic stretching frequencies unambiguously, the C=C stretching frequencies of the coordinated olefins have been tentatively assigned to the values shown in Table I on the basis of the absence of bands in this region for the analogous carbonyl complexes and comparison with spectra of the free ligands. The observed values are typical of olefin complexes in general[5a,15] and Cu(I) complexes in particular.[1,3]

The infrared data for the carbonyl compounds reported here indicate that the overall structure of the complex is different from that of the analogous olefin complex. The split perchlorate band suggests unidentate coordination of the anion.[14] This anion coordination has been confirmed in the structural characterization of $[Cu(NH(py)_2)(CO)ClO_4]$, in which a perchlorate oxygen atom is coordinated to the Cu(I) ion at a rather long distance (2.429 (1) Å).[1] The copper ion is also coordinated to two pyridyl nitrogen atoms and a carbonyl group in a trigonal-planar arrangement. The carbonyl stretching frequencies shown in Table I are somewhat higher than those typically observed for Cu(I) carbonyl complexes, but these values are not unique; rather, values >2100 cm^{-1} appear to be characteristic of complexes with weakly coordinating anions.[1,9,16,17] The carbonyl stretching frequencies reported here are not particularly sensitive to the other ligands in the copper coordination sphere.

Discussion

The Cu(I) complexes with monoolefins and carbon monoxide described here show that the general features suggested by our earlier work[1-3] are general characteristics of Cu(I) coordination chemistry with these small molecules. Previous studies with the ligands $NH(py)_2$,[1,2] hydrotris(1-pyrazolyl)borate, and hydrotris(3,5-dimethyl-1-pyrazolyl)borate[3] suggest that Cu(I)–monoolefin complexes show a preference for the trigonal-planar geometry, although tetrahedral complexes can be prepared with the proper choice of ligand. Carbonyl complexes are generally four-coordinate. The complexes **1**–**16** reported in this study show these same properties. The analytical and spectroscopic data for the monoolefin complexes are consistent with the formation of trigonal-planar, cationic Cu(I) complexes with uncoordinated perchlorate anions. This structure has been confirmed for $[Cu(NH(py)_2)(C_6H_{10})]ClO_4$ (**16**) reported elsewhere.[13] Similarly, the analytical and spectroscopic data for each of the carbonyl complexes suggest formation of a four-coordinate cuprous complex with a unidentate perchlorate group.

The spectroscopic data for the reported ethylene and propylene complexes suggest that metal–olefin bonding interactions are in accord with the scheme suggested previously. The crystal structures of the Cu(I)–monoolefin and -acetylene complexes reveal relatively short carbon–carbon bond distances for the coordinated olefinic or acetylenic bond.[1-3] These results suggest that σ bonding is the dominant interaction between metal and olefin or acetylene; π back-bonding, the dominant interaction for other d^{10} metals such as Ni(0), is not of great importance. The relatively high olefin stretching frequency and the positions of the olefin proton resonances in the NMR spectra for the ethylene and propylene complexes compare with those of the structurally characterized complexes and are consistent with this bonding scheme.

Our work has established some general properties of the Cu(I) coordination chemistry with monoolefin, acetylene, and carbon monoxide and has indicated similarities with, and differences from, the coordination chemistry of other d^{10} metals such as Ni(0). The overall geometrical preferences of Cu(I) and Ni(0) ions with monoolefins and carbon monoxide are identical, but the metal ion–small molecule interactions are different in the two cases. The different effects on the coordinated olefin bond are noted above. This work and others[7,9,16,17] show that Cu(I)–carbonyl complexes tend to be four-coordinate; this tendency is true of Ni(0) complexes as well. However, we have found no example of Cu(I) ions

---

(12) Parshall, G. W. "Homogeneous Catalysis"; Wiley: New York, 1980; pp 22–47.

(13) (a) Thompson, J. S.; Calabrese, J. C.; Whitney, J. F., submitted for publication. (b) The complex $[Cu(NH(py)_2)(C_6H_{10})]ClO_4$ crystallizes in the monoclinic space group $P2_1/c$ with four molecules in a unit cell of dimensions 7.478 (1) Å, 25.014 (6) Å, 9.530 (1) Å, and β = 106.23 (1)° at −100 °C. The geometry about the cuprous ion, which is coordinated to two pyridyl nitrogen atoms and a cyclohexene molecule, is trigonal planar. The perchlorate anion is well displaced from the cation.

(14) Nakamoto, K. "Infrared and Raman Spectra of Inorganic and Coordination Compounds", 3rd ed.; Wiley: New York, 1978; pp 242–243.

(15) Reference 14, pp 383–385.

(16) Doyle, G.; Eriksen, K. A.; Engen, D. V. *Inorg. Chem.* **1983**, *22*, 2892–2895.

(17) (a) Churchill, M. R.; DeBoer, B. G.; Rotella, F. J.; Abu Salah, O. M.; Bruce, M. I. *Inorg. Chem.* **1975**, *14*, 2051–2056. (b) Mealli, C.; Arcus, C. S.; Wilkinson, J. L.; Marks, T. J.; Ibers, J. A. *J. Am. Chem. Soc.* **1976**, *98*, 711–718. (c) Pasquali, M.; Marchetti, F.; Floriani, C. *Inorg. Chem.* **1978**, *17*, 1684–1688. (d) Pasquali, M.; Marini, G.; Floriani, C.; Gaetani-Manfredotti, A.; Guastini, C. *Inorg. Chem.* **1980**, *19*, 2525–2531. (e) Pasquali, M.; Floriani, C.; Gaetani-Manfredotti, A. *Inorg. Chem.* **1981**, *20*, 3382–3388. (f) Pasquali, M.; Floriani, C.; Venturi, G.; Gaetani-Manfredotti, A.; Chiesi-Villa, A. *J. Am. Chem. Soc.* **1982**, *104*, 4092–4099.

coordinating more than one carbonyl group even in a carbon monoxide atmosphere,[18] whereas Ni(0) complexes with two, three, and four carbonyl groups are well-known.[6] These properties of Cu(I)–ethylene and –carbonyl complexes are a manifestation of the poor π-back-bonding ability of cuprous ion relative to that of Ni(0) species. These experimental results are in accord with recent theoretical studies of the bonding of small, unsaturated molecules to cuprous ion.[19]

Registry No. **1**, 93757-51-8; **2**, 93757-53-0; **3**, 93757-55-2; **4**, 93757-56-3; **5**, 93757-58-5; **6**, 93757-60-9; **7**, 93781-70-5; **8**, 93757-62-1; **9**, 93757-64-3; **10**, 93757-66-5; **11**, 93757-67-6; **12**, 93757-69-8; **13**, 93757-71-2; **14**, 93757-73-4; **15**, 93757-74-5; **16**, 93757-76-7; $Cu(ClO_4)_2$, 13770-18-8; Cu, 7440-50-8; C_2H_4, 74-85-1; C_3H_6, 115-07-1; C_6H_{10}, 110-83-8.

---

(18) (a) Kitagawa et al.[18b] have reported the preparation of $[Cu(bpy)(CO)_2]ClO_4$, solely on the basis of ^1H NMR data. We have been unable to isolate this material with our procedure, although our NMR data agree with published values. (b) Kitagawa, S.; Munakata, M.; Miyaji, N. *Inorg. Chem.* **1982**, *21*, 3842–3843.

(19) Sakaki, S.; Kitaura, K.; Morokuma, K. *Inorg. Chem.* **1982**, *21*, 760–765.

Contribution from the Department of Chemistry,
The University of Texas at Austin,
Austin, Texas 78712

Evidence for the Gold Anion in Ethylenediamine

R. Jagannathan, D. B. Wallace, and J. J. Lagowski*

Received May 9, 1984

The dissolution of alkali metals in several types of nonaqueous solvents (amines, ethers, and amides) has been conclusively shown to produce a new species, metal anions, M^- (M = alkali metal).[1] Recent work has led to the isolation of substances incorporating some of these species.[2] Similarly, several post transition elements have been shown to form homonuclear polyatomic cluster anions in ammonia and in ethylenediamine.[3] Among the transition metals, however, gold alone is known to form a metal monoanion (Au^-) in liquid ammonia.[4] We report here spectroscopic and electrochemical evidence for the existence of Au^- in ethylenediamine. Thus, Au^- is the only metal monoanion that exists in liquid ammonia, a solvent in which alkali-metal anions have not been detected to date, and in other solvents such as ethylenediamine in which alkalide anions are known to exist.

Experimental Section

A standard three-electrode configuration was used for electrochemical studies. A platinum button and a wire served as the working and auxiliary electrodes, respectively. A silver wire separated by a double frit was used as the pseudoreference electrode. The Ag-wire pseudoreference electrode was found to be stable during the period of the experiment. It was not possible to obtain standard potentials with ferrocene or cobaltocene because of the instability of the compounds and/or the products of the redox process. Naphthalene however exhibited a quasi-reversible process with $E_{1/2}$ of −2.15 V with reference to the Ag-wire electrode. The standard reduction potential for naphthalene is invariant with solvents and appears at −2.55 ± 0.1 V with reference to the SCE. Electrochemical experiments at 30 °C were performed on a Princeton Applied Research Model 173 potentiostat and Model 175 universal programmer and a Houston Instrument X-Y recorder.

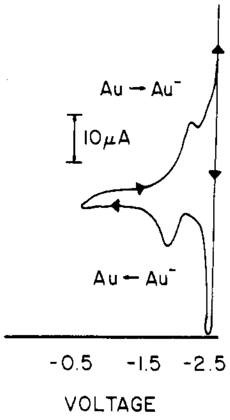

Figure 1. Typical current–voltage plot in ethylenediamine (supporting electrolyte 0.1 M K(crypt) triflate; reference Ag wire; scan rate 200 mV/s).

The supporting electrolyte (0.1 M) was potassium trifluoromethanesulfonate (triflate), which is superior to potassium iodide because it is not susceptible to oxidation. In liquid ammonia, bulk coulometric generation of solvated electrons in a three-compartment cell was performed with potassium iodide and with potassium trifluoromethanesulfonate. With KI, the anode compartment became colored with the formation of iodine and its reaction products with ammonia. In the case of potassium trifluoromethanesulfonate, copious gas evolution was observed at the anode during electrolysis, indicating ammonia oxidation to nitrogen as the predominant process at the anode. Up to 1 mmol of Au^- could be routinely generated electrochemically with 0.1 M potassium trifluoromethanesulfonate electrolyte in liquid ammonia at −50 °C.

Anhydrous ethylenediamine (Fisher Scientific) was refluxed over calcium hydride for 24 h and distilled onto Na–K alloy. After 24 h, this solution was distilled directly into the electrochemical or spectroscopic cell under high vacuum (10^{-4} torr). Experiments in methylamine were performed in a high-pressure cell with an O-ring seal and a pressure stopcock. Methylamine was purified by storing over Na–K alloy (1:1) for 24 h and distilled into the reaction cell.

Results and Discussion

A cyclic voltammogram of the supporting electrolyte in ethylenediamine under prepurified argon at this stage revealed a single electrode process at −2.65 V in the cathodic scan and a return wave on the reverse scan. Holding the potential at −2.7 V resulted in a rapidly disappearing blue coloration around the electrode. Na–K alloy (1:1; 0.1 mL) was then syringed into the cell; the cyclic voltammogram of the resulting deep blue solution was similar to the one obtained earlier, with no additional electrode processes being observed. Gold powder (0.02 g) was then added and the solution vigorously stirred for about 15 min. A positive cyclic voltammetric scan initiated at −2.6 V resulted in an anodic peak at −1.80 V and a cathodic peak at −2.10 V on reversing the scan. A representative cyclic voltammogram is presented in Figure 1. This observation immediately points to the presence of a gold-related species, and comparison with experiments in liquid ammonia[4] suggests that the gold powder was reduced to auride ion ($Au + e^- \rightarrow Au^-$). The anodic peak corresponds to the oxidation of Au^- at the electrode, and the cathodic peak represents the formation of Au^- from freshly deposited gold. The peak separation is about 300 mV, which is larger than in ammonia and suggests a greater kinetic barrier to the electrode process occurring in ethylenediamine. A surface effect was also apparent. Use of a gold plate instead of the powder under similar reaction conditions resulted in similar results, except that longer reaction times were required to produce Au^-; in these cases, competitive solvent decomposition was also observed, which resulted in smaller peak

---

(1) (a) Matalon, S.; Golden, S.; Ottolenghi, M. *J. Phys. Chem.* **1969**, *73*, 3098. (b) Fletcher, J. W.; Seddon, W. A. *J. Phys. Chem.* **1975**, *79*, 3055. (c) Dye, J. L. In "Progress in Macrocyclic Chemistry"; Izatt, R. M., Christensen, J. J., Eds.; Wiley-Interscience: New York, 1979; Vol. I, pp 63–113.

(2) Van Eck, Bradley; Le, Lon Dinh; Issa, Dheek; Dye, James L. *Inorg. Chem.* **1982**, *21*, 1966.

(3) Burns, R. C.; Corbett, J. D. *J. Am. Chem. Soc.* **1981**, *103*, 2627.

(4) (a) Peer, W. J.; Lagowski, J. J. *J. Am. Chem. Soc.* **1978**, *100*, 6260. (b) Teherani, T.; Peer, W. J.; Lagowski, J. J.; Bard, A. J. *J. Am. Chem. Soc.* **1978**, *100*, 7768.

0020-1669/85/1324-0113$01.50/0 © 1985 American Chemical Society