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Carbon Monoxide Absorption by Copper(I) Halides in Organic Solvents: Isolation and Structure of μ-Halogeno-dicopper(I) Carbonyl Complexes

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Copper(I) chloride absorbs, at room temperature and atmospheric pressure, one molecule of carbon monoxide/copper, when suspended in organic solvents like methanol, tetrahydrofuran, and diglymes [$\nu_{CO}(CH_3OH) = 2070\ cm^{-1}$, $\nu_{CO}(thf) = 2085\ cm^{-1}$]. The white crystalline solid called "CuCOCl", while stable in situ at room temperature under a carbon monoxide atmosphere, loses partially CO during its isolation in the solid state [$\nu_{CO}(Nujol) = 2120\ cm^{-1}$]. CuBr reacts very slowly with CO in the same conditions, without reaching the 1/1 Cu/CO molar ratio, while CuI is unreactive. The addition of *N,N,N',N'*-tetramethylethylenediamine, tmen, to a suspension of copper(I) halides, CuX, in methanol under a carbon monoxide atmosphere, produces colorless solutions (ν_{CO} = ca. 2060–2070 cm^{-1}) from which $[Cu_2(tmen)_2(CO)_2X](BPh_4)$ can be isolated as white crystals [ν_{CO}(Nujol): X = Cl, 2065; X = Br, 2070; X = I, 2063 and 2073 cm^{-1}]. X-ray analyses were performed on the three isostructural complexes, which contain the bent OC–Cu–X–Cu–CO framework with the Cu–X–Cu angle varying as follows: X = Cl, 103.0 (1)°; X = Br, 102.8 (1)°; X = I, 105.1 (1)°. tmen completes the pseudotetrahedral coordination around each copper atom. Cu–C, C–O, and Cu–N bond distances are practically independent of the halogen, whose influence can be recognized on the following parameters: (i) Cu···Cu separation in the dimer [X = Cl, 3.643 (2); X = Br, 3.827 (2); X = I, 4.141 (3) Å]; (ii) the relative arrangement of the two CO's of the dimer, specified with the torsional angle ϕ reported in Figure 2. The bridging mode displayed by X does not affect significantly the Cu–X bond distances [X = Cl, 2.328 (2); X = Br, 2.448 (2); X = I, 2.609 (2) Å (mean values)], which fall in the range of doubly bridged or terminal Cu–X bonds. $[Cu_2(tmen)_2(CO)_2X](BPh_4)$ complexes crystallize in the triclinic space group $P\bar{1}$ with $Z = 2$. The other crystallographic details are as follows. For X = Cl: $a = 14.179$ (2), $b = 15.525$ (2), $c = 9.399$ (1) Å; $\alpha = 82.49$ (2), $\beta = 89.19$ (2), $\gamma = 80.06$ (2)°; $V = 2020.4$ (5) Å^3. The final R factor was 6.1% for the 5967 observed reflections. For X = Br: $a = 14.049$ (2), $b = 15.628$ (2), $c = 9.371$ (1) Å; $\alpha = 82.35$ (2), $\beta = 88.68$ (2), $\gamma = 79.52$ (2)°; $V = 2005.2$ (5) Å^3. The final R factor was 6.9% for 2725 observed reflections. For X = I: $a = 14.019$ (5), $b = 15.946$ (5), $c = 9.411$ (6) Å; $\alpha = 82.60$ (3), $\beta = 88.23$ (5), $\gamma = 78.44$ (4)°; $V = 2044.0$ (2) Å^3. The final R factor was 6.7% for 2742 observed reflections.

Introduction

Copper(I)–carbon monoxide chemistry is one of the oldest areas in coordination chemistry experiencing a renaissance as a consequence of the interest in metal-promoted carbon monoxide transformations. The utilization of copper(I)-containing heterogeneous catalysts[1] active in carbon monoxide activation contrasts with the very scanty information available on carbon monoxide bonded to copper(I) in simple complexes.[2] The utilization of copper(I) complexes as electrophilic promotors of carbon monoxide is the obvious consequence of the chemical properties of copper(I) and of the rather high CO stretching frequency of CO bonded to copper(I).[2–6]

A systematic search is being made in our laboratories to identify ligand systems which promote the coordination and the activation of carbon monoxide by copper(I).[3–6] The present report concerns the interaction of carbon monoxide with copper(I) halides in organic solvents, which are currently used in organometallic and coordination chemistry, and the isolation of related complexes.

It has been well-known for over 1 century that hydrochloric acid solutions of copper(I) chloride react with carbon monoxide.[2,7] In spite of many attempts, the isolation of a well-defined solid from these solutions was always unsuccessful,[2] and the nature of the so-called "CuCOCl" must still be clarified.[8–10] Moreover, the utilization of "CuCOCl"[2,8,9] generated in hydrochloric acid solutions is very limited for synthetic purposes.

We describe here the synthesis carried out in organic solvents (methanol, tetrahydrofuran, and diglymes) of the so-called "CuCOCl" which can be used in situ for reactions with organic ligands. By this route, the synthesis of dimeric carbonyl complexes containing the OC–Cu–X–Cu–CO (X = Cl, Br, I) framework is achieved. Their structure and properties are relevant not only to copper(I) chemistry but also to the general context of transition-metal chemistry, where metals rarely are bridged by a single halogen.[11] A brief account of this work was recently reported.[7]

Experimental Section

Syntheses were carried out under an atmosphere of purified nitrogen. Methanol, tetrahydrofuran (thf), and *N,N,N',N'*-tetramethylethylenediamine (tmen) were dried and distilled before use. CuCl, CuBr, and CuI were prepared by published procedures.[12] Infrared spectra were recorded with a Perkin-Elmer 282 spectrophotometer.

Absorption of CO by CuCl. (a) Methanol as Solvent. CuCl (2.0 g, 20.2 mmol) suspended in methanol very rapidly absorbs carbon monoxide at room temperature and atmospheric pressure. A noticeable change in the shape of the solid occurs during the absorption, and the methanolic solution has a CO band at 2070 cm^{-1}. The solid [1.7

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(1) Weissermel, K.; Arpe, H. J. "Industrial Organic Chemistry"; Verlag: Weinheim, 1978, Chapter 2.

(2) Bruce, M. I. *J. Organomet. Chem.* **1972**, *44*, 209. This review covers the literature up to 1970.

(3) Churchill, M. R.; De Boer, B. G.; Rotella, F. J.; Abu Salah, O. M.; Bruce, M. I. *Inorg. Chem.* **1975**, *14*, 2051. Tsuda, T.; Habu, H.; Horiguchi, S.; Saegusa, T. *J. Am. Chem. Soc.* **1974**, *96*, 5930. Gagné, R. R.; Allison, J. L.; Gall, R. S. Koval, K. A. *Ibid.* **1979**, *99*, 7170. Scott, A. F.; Wilkening, L. L.; Rubin, B. *Inorg. Chem.* **1969**, *10*, 2533; Ogura, T. *Ibid.* **1976**, *15*, 2301. Desjardins, C. D.; Edwards, D. B.; Passinore, *J. Can. J. Chem.* **1979**, *57*, 2714 and references cited therein.

(4) Pasquali, M.; Marchetti, F.; Floriani, C. *Inorg. Chem.* **1978**, *17*, 1684.

(5) Pasquali, M.; Floriani, C.; Gaetani-Manfredotti, A. *J. Chem. Soc., Chem. Commun.* **1978**, 921; *Inorg. Chem.* **1980**, *19*, 1191.

(6) Pasquali, M.; Floriani, C.; Gaetani-Manfredotti, A.; Guastini, C. *J. Chem. Soc., Chem. Commun.* **1979**, 197; *Inorg. Chem.* **1980**, *19*, 2525.

(7) Pasquali, M.; Marini, G.; Floriani, C.; Gaetani-Manfredotti, A. *J. Chem. Soc., Chem. Commun.* **1979**, 937.

(8) Backen, W.; Vestin, R. *Acta Chem. Scand., Ser. A* **1979**, *A33*, 85 and references cited therein. Busch, M. A.; Franklin, T. C. *Inorg. Chem.* **1979**, *18*, 521 and references cited therein.

(9) Hieber, W.; Behrens, H.; Teller, U. *Z. Anorg. Allg. Chem.* **1942**, *249*, 26. Cotton, F. A.; Wilkinson, G. "Advanced Inorganic Chemistry", 3rd ed.; Interscience: New York, 1972; p 911.

(10) A report of the not further confirmed isolation of $[CuClCO]\cdot 2H_2O$ is given in: Keller, R. N.; Wycoff, H. D. *Inorg. Synth.* **1946**, *2*, 4.

(11) Handy, L. B.; Ruff, J. K.; Dahl, L. F. *J. Am. Chem. Soc.* **1970**, *92*, 7327 and references cited therein.

(12) Brauer, G. "Handbook of Preparative Inorganic Chemistry", 2nd ed.; Academic Press: New York, 1965; Vol. 2, pp 1005–1007.

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g, ν_{CO}(Nujol) = 2120 cm^{-1}] loses CO during its isolation, notwithstanding that all the operations, including drying are carried out in a carbon monoxide atmosphere and at 0 °C. It gives 0.60 mol of CO/copper by the reaction with $P(OEt)_3$ in thf.

CuCl (0.144 g, 1.45 mmol) in methanol (20 mL) absorbs at 16.7° C 39.3 mL of carbon monoxide in 15 min, corresponding to a CO/Cu molar ratio = 0.95.

(b) thf as Solvent. CuCl (2.0 g, 20.2 mmol) suspended in thf absorbs carbon monoxide at room temperature and atmospheric pressure, producing a solution from which a white crystalline solid suddenly precipitates. The solution shows a CO band at 2085 cm^{-1}. The solid was filtered and dried in a stream of carbon monoxide. It loses completely CO in vacuo or under a N_2 atmosphere even at 0 °C. The solid displays (Nujol) a CO band at 2120 cm^{-1} and shows the presence of thf.

CuCl (0.116 g, 1.17 mmol) in 20 mL of thf at 16.8 °C absorbs 31.5 mL of CO (1.10 mmol) in 23 min, corresponding to a CO/Cu molar ratio = 0.94.

(c) Diglymes (Ethylene Glycol–Dimethyl Ether, Diethylene Glycol–Dimethyl Ether) as Solvents. The reaction of CuCl with CO in these solvents gives results very similar to those observed in thf.

(d) Benzene as Solvent. CuCl (0.105 g, 1.06 mmol) in benzene (20 mL) at 16.5 °C very slowly absorbs (18 h) carbon monoxide (0.69 mmol).

Absorption of CO by CuBr. CuBr (0.145 g, 1.01 mmol) suspended in methanol (20 mL) absorbs 0.25 mmol of CO in 12 h.

No absorption of CO by CuI is observed under the same conditions.

Synthesis of [Cu_2(tmen)$_2$(CO)$_2$Cl](BPh_4). The solid formed by carbonylation of CuCl (1.05 g, 10.6 mmol) in methanol (30 mL) at room temperature dissolves with addition of tmen (1.6 mL, 10.60 mmol) dissolved in the same solvent (20 mL) (ν_{CO} = 2070 cm^{-1}). The solution obtained gives white crystals of [Cu_2(tmen)$_2$(CO)$_2$Cl](BPh_4) [ca. 30%, ν_{CO}(Nujol) = 2065 cm^{-1}] upon the addition of $NaBPh_4$ (3.7 g, 10.8 mmol) dissolved in methanol (20 mL). Anal. Calcd for $C_{38}H_{52}N_4O_2BClCu_2$: C, 59.26; H, 6.80, N, 7.27; Cl, 4.60. Found: C, 58.51; H, 6.90; N, 7.18; Cl, 4.61.

Synthesis of [Cu_2(tmen)$_2$(CO)$_2$Br](BPh_4). A CuBr (1.0 g, 6.97 mmol) suspension in methanol (40 mL) containing tmen (2.5 mL, 16.56 mmol) reacts with CO at room temperature and atmospheric pressure, producing a colorless solution (broad CO band centered at 2058 cm^{-1}) from which [Cu_2(tmen)$_2$(CO)$_2$Br](BPh_4) [ca. 30%, ν_{CO}(Nujol) = 2070 cm^{-1}] crystallizes out by addition of $NaBPh_4$ (2.5 g, 7.31 mmol). Anal. Calcd for $C_{38}H_{52}N_4O_2BBrCu_2$: C, 56.02; H, 6.43; N, 6.88; Br, 9.81. Found: C, 56.24; H, 6.68; N, 7.21; Br, 10.24.

Synthesis of [Cu_2(tmen)$_2$(CO)$_2$I](BPh_4). A methanolic solution (40 mL) of tmen (3 mL, 19.88 mmol) is added to CuI (1.50 g, 7.87 mmol) suspended in methanol (40 mL). The reaction with CO dissolves the solid, producing a colorless solution (ν_{CO} = 2070 cm^{-1}) with few undissolved solid, which is filtered out in a CO atmosphere. When the solution is filtered in a flask containing $NaBPh_4$ (3.60 g, 10.52 mmol), a crystalline white solid forms [ca. 30%, ν_{CO}(Nujol) = 2063 and 2073 cm^{-1}]. Anal. Calcd for $C_{38}H_{52}N_4O_2BICu_2$: C, 52.97; H, 6.08; N, 6.50; I, 14.73. Found: C, 53.90; H, 6.50; N, 6.63; I, 15.17.

Collection and Reduction of the X-ray Data. Preliminary X-ray examination (rotation and Weissenberg photographs) revealed that the three compounds are triclinic and isostructural. Crystal data and details of data collection are listed in Table I. Cell dimensions were obtained by least-squares refinements of the 2θ values of 20 reflections ($2\theta > 100°$ for $C_{38}H_{52}BClCu_2N_4O_2$, $2\theta > 30°$ for $C_{38}H_{52}BBrCu_2N_4O_2$ and $C_{38}H_{52}BCu_2IN_4O_2$). The crystals used for data collection, sealed in glass capillaries, were mounted with the [001] axis along the ϕ axis of the diffractometer. Intensities were collected on the "on line" single-crystal automated Siemens AED diffractometer. The pulse height discriminator was set to accept 90% of the incident radiation. The moving-counter–moving-crystal scan technique was used with a drive speed related to the number of counts on the peak (lowest speed 2.5°/min). A standard reflection, monitored after 20 reflections, showed an irregular decreasing in intensity totaling ca. 20%, 8%, and 15% for chlorine, bromine, and iodine derivatives, respectively. Since differences in intensities, probably due both to some crystal decay, instability of apparatus, or crystal movement, were small ($<\sigma(I)$) within each set, all the data were corrected by applying to the intensities of each set of 20 reflections a scale factor $p = I_{ref}/1/2(I_1 + I_2)$, where I_{ref} is the starting intensity of the standard reflection, I_1 and I_2 are the intensities of this reflection measured before and after each set.

Table I. Summary of the Crystal Data and Intensity Collection

	$C_{38}H_{52}$-$BClCu_2N_4O_2$	$C_{38}H_{52}$-$BBrCu_2N_4O_2$	$C_{38}H_{52}$-$BCu_2IN_4O_2$
a, Å	14.179 (2)	14.049 (2)	14.019 (5)
b, Å	15.525 (2)	15.628 (2)	15.946 (5)
c, Å	9.399 (1)	9.371 (1)	9.411 (6)
α, deg	82.49 (2)	82.35 (2)	82.60 (3)
β, deg	89.19 (2)	88.68 (2)	88.23 (5)
γ, deg	80.06 (2)	79.52 (2)	78.44 (4)
Z	2	2	2
M_r	770.2	814.7	861.7
d(calcd), g cm^{-3}	1.266	1.349	1.400
space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
radiation	Ni-filtered Cu Kα (λ 1.541 78 Å)	Nb-filtered Mo Kα (λ 0.710 69 Å)	Nb-filtered Mo Kα (λ 0.710 69 Å)
μ, mm^{-1}	2.16	2.08	1.82
$\mu\bar{r}$	0.6	0.2	0.2
scan type	θ–2θ	θ–2θ	θ–2θ
scan range	±0.5° from peak center		
scan speed	2.5–10° θ/min		
bkgd	stationary cryst at ±0.5°		
2θ limits, deg	6–140	5–44	5–44
criterion for obsn	$I > 2\sigma(I)$	$I > 2\sigma(I)$	$I > 2\sigma(I)$
unique obsd data	5969	2726	2742
unique total data	7662	4904	4260
cryst dimens, mm	0.66 × 0.48 × 0.64	0.36 × 0.06 × 0.55	0.48 × 0.05 × 0.51

For intensities and backgrounds the "five point" technique[13] was used. Corrections were applied to the data for Lorentz and polarization factors. The effects for absorption were judged to be minimal ($\mu\bar{r}$ = 0.2) for bromine and iodine derivatives and were not compensated for. No absorption correction could be applied to chlorine derivative ($\mu\bar{r}$ = 0.6) due to irregular shape of the crystal and difficulties in indexing crystal faces. Thermal coefficients are therefore influenced by this omission.

Solution and Refinement of the Structures.[14] The three structures were solved by conventional techniques and refined by least-squares methods minimizing the function $\sum w|F_o - F_c|^2$, first by unit weights and then by weighting according to the scheme $w = k/(\sigma^2(F_o) + \text{abs}(g)[F_o^2])$ based on counting statistics. The error in observation of unit weight is 1.32, 0.93, and 1.13, respectively, for chlorine, bromine, and iodine compounds. k is redetermined after each structure factor calculation and refined by fitting $(F_o - F_c)^2$ to $(\sigma^2(F_o) + \text{abs}(g)[F_o^2])/k$. The values for g were those giving the smallest variation of the mean value of $w(F_o - F_c)^2$ as a function of the magnitude of F_o. In final refinements k = 1.0000 for the three compounds and g = 0.002, 0.005, and 0.003 for chlorine, bromine, and iodine derivatives, respectively. Anomalous scattering corrections were included in all structure factor calculations. No evidence for secondary extinction was found. In the last cycle of least-squares refinements no parameter shifted by more than 0.3σ. The scattering factors from ref 15 were used for Cu and I, those of Cromer and Mann[16] for Br, Cl, O, N, C, and B, and those of Stewart, Davidson, and Simpson[17] for H. Tables of observed and calculated structure factors and isotropic and anisotropic thermal parameters are available as supplementary material. The final atomic parameters are listed in Tables II–IV. A more detailed description of the three structure determinations will be given in the following.

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(13) Hoppe, W. *Acta Crystallogr., Sect. A* **1969**, *A25*, 67.

(14) Computer programs used on a Cyber 7600 computer of the Centro di Calcolo Interuniversitario dell'Italia Nord-Orientale (Casalecchio, BO) were those of the Sheldrick's SHELX-76 system (University of Cambridge, Cambridge England, 1976). Calculations were performed with the financial support of the University of Parma.

(15) "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV, p 99.

(16) Cromer, D. T.; Mann, J. B. *Acta Crystallogr., Sect. A* **1968**, *A24*, 321.

(17) Stewart, R. F.; Davidson, E. R.; Simpson, W. T. *J. Chem. Phys.* **1965**, *42*, 3175.

Table II. Fractional Atomic Coordinates $\times 10^4$ for $[Cu_2(tmen)_2(CO)_2Cl](BPh_4)$

atom	*x/a*	*y/b*	*z/c*	atom	*x/a*	*y/b*	*z/c*
Cu(1)	2718 (1)	2822 (1)	2195 (1)	C(21)	2969 (2)	7251 (2)	5365 (3)
Cu(2)	2901 (1)	600 (1)	1238 (1)	C(22)	3350 (2)	7073 (2)	4020 (4)
Cl	2503 (1)	2059 (1)	258 (1)	C(23)	4027 (2)	7520 (2)	3330 (4)
O(13)	2890 (4)	1783 (3)	5031 (5)	C(24)	4346 (2)	8177 (3)	3942 (5)
O(14)	4586 (3)	362 (3)	3062 (7)	C(25)	3970 (3)	8398 (3)	5198 (5)
N(1)	1708 (2)	3974 (2)	1860 (4)	C(26)	3291 (2)	7938 (2)	5931 (4)
N(2)	3761 (2)	3597 (2)	1481 (4)	C(31)	1215 (2)	6962 (2)	5161 (3)
N(3)	2768 (3)	−137 (2)	−452 (4)	C(32)	707 (2)	7828 (2)	5035 (4)
N(4)	1639 (2)	189 (2)	2050 (5)	C(33)	−109 (3)	8105 (3)	4181 (5)
C(1)	2284 (3)	4675 (3)	1643 (8)	C(34)	−437 (2)	7539 (3)	3384 (5)
C(2)	3171 (3)	4415 (3)	798 (7)	C(35)	43 (2)	6691 (3)	3453 (4)
C(3)	1810 (6)	−377 (4)	−249 (8)	C(36)	858 (2)	6411 (2)	4322 (4)
C(4)	1553 (4)	−545 (4)	1283 (10)	C(41)	2619 (2)	5613 (2)	6277 (3)
C(5)	1113 (3)	4013 (4)	584 (6)	C(42)	2037 (2)	4978 (2)	6701 (4)
C(6)	1064 (4)	4075 (4)	3104 (7)	C(43)	2388 (3)	4085 (2)	6869 (4)
C(7)	4432 (3)	3245 (4)	389 (6)	C(44)	3344 (3)	3773 (2)	6651 (4)
C(8)	4333 (4)	3744 (5)	2694 (7)	C(45)	3932 (2)	4372 (2)	6278 (4)
C(9)	3528 (6)	−939 (3)	−342 (7)	C(46)	3581 (2)	5269 (2)	6074 (4)
C(10)	2817 (6)	344 (4)	−1886 (6)	C(51)	2010 (2)	6875 (2)	7809 (3)
C(11)	805 (4)	897 (4)	1907 (8)	C(52)	2782 (2)	6727 (2)	8769 (4)
C(12)	1727 (4)	−160 (4)	3594 (8)	C(53)	2688 (2)	6852 (2)	10203 (4)
C(13)	2822 (4)	2186 (3)	3929 (6)	C(54)	1789 (3)	7138 (2)	10752 (4)
C(14)	3931 (3)	431 (3)	2326 (6)	C(55)	1015 (3)	7272 (2)	9843 (4)
E(1)	2195 (2)	6677 (2)	6148 (4)	C(56)	1117 (2)	7151 (2)	8416 (4)

Table III. Fractional Atomic Coordinates $\times 10^4$ for $[Cu_2(tmen)_2(CO)_2Br](BPh_4)$

atom	*x/a*	*y/b*	*z/c*	atom	*x/a*	*y/b*	*z/c*
Cu(1)	2755 (1)	2870 (1)	2198 (1)	C(21)	2961 (6)	7268 (6)	5363 (9)
Cu(2)	2901 (1)	550 (1)	1214 (1)	C(22)	3360 (7)	7077 (6)	4013 (10)
Br	2520 (1)	2075 (1)	160 (1)	C(23)	4031 (7)	7497 (7)	3328 (11)
O(13)	2975 (9)	1766 (7)	4966 (11)	C(24)	4345 (8)	8137 (8)	3900 (13)
O(14)	4576 (9)	358 (8)	3063 (17)	C(25)	3951 (9)	8366 (7)	5218 (13)
N(1)	1739 (6)	4011 (6)	1951 (10)	C(26)	3287 (7)	7919 (7)	5911 (10)
N(2)	3777 (6)	3646 (6)	1511 (9)	C(31)	1202 (7)	6984 (7)	5161 (9)
N(3)	2799 (10)	−192 (6)	−447 (10)	C(32)	668 (8)	7841 (7)	5055 (11)
N(4)	1649 (7)	173 (6)	2030 (11)	C(33)	−132 (8)	8125 (7)	4197 (12)
C(1)	2277 (10)	4697 (8)	1789 (19)	C(34)	−464 (8)	7546 (9)	3407 (12)
C(2)	3166 (10)	4483 (9)	905 (17)	C(35)	28 (8)	6708 (9)	3461 (11)
C(3)	1843 (19)	−429 (12)	−224 (19)	C(36)	852 (7)	6429 (7)	4352 (10)
C(4)	1533 (11)	−573 (10)	1231 (26)	C(41)	2601 (7)	5627 (6)	6273 (8)
C(5)	1114 (10)	4133 (11)	712 (15)	C(42)	2024 (7)	5023 (7)	6748 (10)
C(6)	1092 (9)	4073 (8)	3238 (13)	C(43)	2365 (8)	4137 (7)	6926 (11)
C(7)	4449 (10)	3340 (10)	379 (14)	C(44)	3321 (10)	3810 (7)	6686 (10)
C(8)	4361 (9)	3746 (12)	2712 (15)	C(45)	3929 (8)	4391 (7)	6273 (11)
C(9)	3527 (14)	−955 (10)	−330 (15)	C(46)	3553 (7)	5287 (6)	6068 (10)
C(10)	2795 (14)	291 (10)	−1890 (15)	C(51)	1972 (7)	6897 (6)	7818 (9)
C(11)	812 (12)	836 (10)	1903 (20)	C(52)	2777 (7)	6742 (6)	8779 (10)
C(12)	1746 (11)	−179 (11)	3617 (17)	C(53)	2642 (8)	6885 (7)	10208 (10)
C(13)	2896 (10)	2195 (8)	3937 (15)	C(54)	1766 (9)	7136 (6)	10752 (10)
C(14)	3912 (11)	403 (9)	2334 (17)	C(55)	978 (9)	7262 (7)	9866 (11)
E(1)	2176 (8)	6692 (7)	6142 (11)	C(56)	1086 (8)	7146 (7)	8415 (10)

$[Cu_2(tmen)_2(CO)_2Cl](BPh_4)$. Initial coordinates for the two independent copper atoms were obtained from a three-dimensional Patterson synthesis. A successive Fourier map yielded the positions of all nonhydrogen atoms. Two cycles of full-matrix least squares with individual isotropic thermal parameters reduced R to 17.9%. Anisotropic refinement of the atoms associated to the cation was performed with cycles of blocked least squares in which, owing to the large number of parameters, the phenyl rings of the BPh_4^- anion were refined as "rigid groups" with free isotropic thermal factors, down to $R = 10.2\%$. At this stage all nonhydrogen atoms were allowed to refine anisotropically and the R value improved to 8.0%. Two subsequent Fourier maps revealed all hydrogen atoms which were introduced in the calculations with isotropic thermal parameters and refined in a cycle. After two further blocked cycles (two blocks) for nonhydrogen atoms, the refinement converged to the final R value of 6.1% ($R_w = 6.8\%$) for 5967 observed reflections, two reflections (200, $0\bar{1}1$) affected by counting errors being rejected. A final difference map showed no peaks with electron density greater than 0.2 e/Å^3.

$[Cu_2(tmen)_2(CO)_2Br](BPh_4)$. The refinement was carried out by starting from the coordinates of the nonhydrogen atoms taken from the isostructural chlorine-containing compound. Two cycles of isotropic full-matrix least squares, in which the phenyl rings of the BPh_4^- anion were considered as "rigid groups", brought R to 17.6%. The refinement was then continued anisotropically by successive cycles of "blocked" (two blocks) least squares down to $R = 7.8\%$. The hydrogen atoms were introduced in calculated positions as fixed-atom contributions in the successive refinement ($U_{iso} = 0.08$ Å^2). The final R value is 6.9% ($R_w = 6.8\%$) for 2725 unique observed data (one reflection, 200, affected by counting errors was rejected). A final difference Fourier map revealed two peaks of ca. 0.8 e/Å^3 at ca. 1 Å from bromine on the Br–Cu lines. No other peak exceeded 0.4 e/Å^3.

$[Cu_2(tmen)_2(CO)_2I](BPh_4)$. Initial coordinates for the nonhydrogen atoms were those of $[Cu_2(tmen)_2(CO)_2Cl](BPh_4)$. The structure was refined by full-matrix least squares, first isotropically (the phenyl rings of the BPh_4^- anion were considered as "rigid groups") and then anisotropically (four cycles), down to $R = 7.6\%$. The hydrogen atoms were put in idealized positions and introduced as fixed atom contributions in the subsequent calculations ($U_{iso} = 0.08$ Å^2). The final discrepancy R index was 6.7% ($R_w = 6.7\%$), considering the unique observed data (Table I). One reflection (200), affected by counting

Table IV. Fractional Atomic Coordinates $\times 10^4$ for $[Cu_2(tmen)_2(CO)_2I](BPh_4)$

atom	*x/a*	*y/b*	*z/c*	atom	*x/a*	*y/b*	*z/c*
Cu(1)	2821 (1)	2943 (1)	2181 (2)	C(21)	2951 (6)	7242 (6)	5381 (12)
Cu(2)	2928 (1)	468 (1)	1199 (2)	C(22)	3329 (7)	7076 (6)	4042 (13)
I	2611 (1)	2067 (1)	69 (1)	C(23)	4042 (7)	7467 (7)	3320 (12)
O(13)	3016 (9)	1802 (8)	4882 (13)	C(24)	4358 (7)	8083 (7)	3935 (16)
O(14)	4546 (9)	282 (8)	3168 (16)	C(25)	4001 (9)	8312 (7)	5222 (16)
N(1)	1742 (6)	4062 (5)	1997 (10)	C(26)	3296 (7)	7895 (6)	5926 (12)
N(2)	3809 (6)	3749 (5)	1524 (10)	C(31)	1167 (7)	7016 (6)	5180 (11)
N(3)	2813 (10)	−286 (6)	−435 (12)	C(32)	662 (7)	7856 (7)	5070 (11)
N(4)	1660 (7)	108 (6)	2046 (13)	C(33)	−168 (9)	8157 (9)	4211 (14)
C(1)	2291 (9)	4747 (7)	1855 (18)	C(34)	−491 (8)	7587 (10)	3429 (15)
C(2)	3182 (10)	4549 (8)	1002 (17)	C(35)	−8 (8)	6764 (10)	3498 (13)
C(3)	1868 (17)	−512 (12)	−190 (24)	C(36)	810 (7)	6473 (7)	4369 (12)
C(4)	1573 (12)	−600 (11)	1290 (29)	C(41)	2568 (7)	5674 (6)	6285 (10)
C(5)	1117 (10)	4190 (10)	792 (15)	C(42)	1981 (7)	5069 (7)	6778 (12)
C(6)	1139 (9)	4073 (9)	3319 (15)	C(43)	2299 (9)	4218 (7)	6965 (12)
C(7)	4472 (9)	3478 (10)	307 (15)	C(44)	3267 (10)	3863 (7)	6689 (12)
C(8)	4402 (9)	3804 (11)	2700 (16)	C(45)	3879 (8)	4409 (7)	6259 (12)
C(9)	3620 (15)	−1017 (10)	−316 (17)	C(46)	3542 (7)	5283 (7)	6039 (10)
C(10)	2829 (12)	148 (10)	−1878 (19)	C(51)	1954 (7)	6925 (5)	7816 (11)
C(11)	798 (10)	778 (10)	1926 (21)	C(52)	2717 (7)	6764 (6)	8839 (16)
C(12)	1732 (12)	−211 (11)	3558 (23)	C(53)	2588 (9)	6888 (6)	10227 (14)
C(13)	2966 (10)	2268 (9)	3871 (18)	C(54)	1679 (9)	7157 (6)	10767 (12)
C(14)	3952 (11)	308 (8)	2414 (18)	C(55)	928 (8)	7277 (6)	9830 (18)
E(1)	2156 (7)	6720 (7)	6152 (14)	C(56)	1031 (7)	7200 (6)	8413 (14)

errors, was rejected. The final difference Fourier map showed no unusual features, the two highest residual peaks being ca. 1 e/Å^3 at ca. 1 Å from iodine on the I–Cu lines. No other peak exceeded 0.6 a/Å^3.

Results and Discussion

Copper(I) halides absorb carbon monoxide at atmospheric pressure in organic solvents at room temperature, the CO/Cu molar ratio depending on the nature of the halide and of the solvent used. The synthetic usefulness of this result deserves a detailed presentation.

CuCl suspended in solvents like methanol, tetrahydrofuran (thf), or diglymes, absorbs reversibly 1 mol of CO/mol of CuCl (eq 1). At the end of the absorption a white crystalline solid

$$\mathrm{CuCl + CO \rightleftarrows \text{“}\underset{I}{CuCOCl}\text{”}} \qquad (1)$$

forms. The carbonyl species, which is partially soluble, displays a CO stretching band at 2070 cm^{-1} (CH_3OH) and at 2085 cm^{-1} (thf), while the solid, independently of the origin, has a CO band at 2120 cm^{-1} (Nujol). It must be noticed that CuCl absorbs, although very slowly, CO even in noncoordinating solvents such as benzene. Any attempt to isolate the pure carbonyl (I) in the solid state fails, since it partially loses its content of carbon monoxide, though all the operations are carried out at 0 °C and in a stream of carbon monoxide. The isolated solid has a variable content of CO and of solvent, as deduced from the IR spectrum and analytical data. Decomposition of I in situ under an atmosphere of CO with $P(OEt)_3$ gives 1 molecule of CO/copper atom. This suggests that “CuCOCl” exists only in situ under an atmosphere of carbon monoxide. Reaction 1 occurs slowly and by a much lesser extent for CuBr and is, practically, not observed for CuI in the same solvents. This trend is parallel to that already observed for the same halides, under highly different experimental conditions.[2] The significant difference in the CO stretching vibration between solid state and solution for I would be a consequence of a different coordination environment around copper(I). The CO stretching vibration at 2070 (CH_3OH) and 2085 cm^{-1} (thf) is on behalf of the tetracoordination around copper(I) in solution. This is mainly suggested by the CO stretching frequencies of copper(I) carbonyls isolated in the solid state, where copper(I) has three basic donor atoms around itself.[2-7] The increase in the CO frequency is parallel to the decrease in the coordination number, so copper(I) is expected to have a lower, even if not defined, coordination number in I in the solid state.

We would emphasize the interest in reaction 1. All previous reports on the carbonylation of CuX in various conditions suggest that the driving force of the reaction could be the ionization of the copper(I)–halide bond.[2,8] The experimental conditions discussed above show that this is not the case. The simultaneous existence around copper(I) of the halide ligand and CO is compatible (vide infra). The “CuCOCl” prepared in organic solvents as reported in reaction 1 can be properly used for the synthesis of organometallic and coordination complexes of copper(I). In this sense, I can be considered a source either of copper(I), nondisproportionating to copper(II) because of the presence of carbon monoxide, or of the [“CuCO”]$^+$ unit.

The isolation of copper(I)–carbonyl halides was successful when the carbonylation of copper(I) halides was carried out in the presence of *N,N,N′,N′*-tetramethylethylenediamine (tmen), as reported in reactions 2 and 3. Complexes III

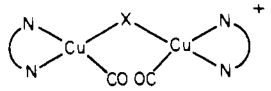
$$\text{2“CuCOCl”} + \text{2tmen} \xrightarrow[+\mathrm{NaBPh_4}]{-\mathrm{NaCl}} \underset{\mathrm{III}}{[\mathrm{Cu_2(tmen)_2(CO)_2Cl}](\mathrm{BPh_4})} \qquad (2)$$

$$\mathrm{2CuX + 2tmen + 2CO} \xrightarrow[+\mathrm{NaBPh_4}]{-\mathrm{NaX}} \underset{\mathrm{III}}{[\mathrm{Cu_2(tmen)_2(CO)_2X}](\mathrm{BPh_4})} \qquad (3)$$

$$(\mathrm{X = Br,I})$$

[ν_{CO}(nujol): X = Cl, 2065; X = Br, 2070; X = I, 2063 and 2073 cm^{-1}] display a rather high stability in the solid state with regard to the loss of CO. The isolation of III deserves some comments related to the following points: (i) the utilization of tmen instead of ethylenediamine (en) in reactions 2 and 3; (ii) the solution–solid state relationship for the carbonylated species.

The structure, which was determined by an X-ray analysis, will help the understanding of the genesis of complexes III.

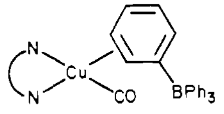


$[Cu_2(tmen)_2(CO)_2X]^+$
(X = Cl, Br, I)

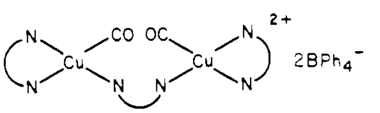
Table V. Interatomic Distances (Å) in the Cation $[Cu_2(tmen)_2(CO)_2X]^+$

	X		
atoms	Cl	Br	I
Cu(1)-X	2.348 (2)	2.472 (2)	2.628 (3)
Cu(2)-X	2.308 (2)	2.424 (2)	2.590 (2)
Cu(1)-N(1)	2.081 (3)	2.062 (8)	2.087 (8)
Cu(1)-N(2)	2.112 (3)	2.081 (9)	2.100 (9)
Cu(2)-N(3)	2.104 (4)	2.083 (10)	2.099 (12)
Cu(2)-N(4)	2.102 (3)	2.055 (10)	2.081 (10)
Cu(1)-C(13)	1.786 (5)	1.814 (13)	1.795 (15)
Cu(2)-C(14)	1.757 (5)	1.748 (16)	1.820 (16)
Cu(1)···Cu(2)	3.643 (2)	3.827 (2)	4.141 (3)
C(13)-O(13)	1.134 (7)	1.094 (17)	1.124 (19)
C(14)-O(14)	1.148 (7)	1.155 (20)	1.102 (22)
N(1)-C(1)	1.462 (6)	1.411 (17)	1.448 (16)
N(2)-C(2)	1.470 (5)	1.479 (15)	1.434 (14)
C(1)-C(2)	1.502 (7)	1.494 (21)	1.466 (20)
N(1)-C(5)	1.465 (6)	1.443 (17)	1.423 (17)
N(1)-C(6)	1.481 (7)	1.496 (15)	1.482 (16)
N(2)-C(7)	1.482 (6)	1.473 (16)	1.504 (16)
N(2)-C(8)	1.472 (8)	1.449 (17)	1.426 (18)
N(3)-C(3)	1.473 (10)	1.460 (30)	1.445 (28)
N(4)-C(4)	1.449 (9)	1.501 (23)	1.436 (25)
C(3)-C(4)	1.481 (12)	1.423 (30)	1.438 (34)
N(3)-C(9)	1.493 (7)	1.417 (19)	1.448 (20)
N(3)-C(10)	1.460 (7)	1.458 (16)	1.444 (20)
N(4)-C(11)	1.464 (6)	1.415 (17)	1.440 (16)
N(4)-C(12)	1.480 (8)	1.516 (18)	1.448 (24)

When in reaction 2 tmen is replaced by en, the complexes $[Cu(en)(CO)(BPh_4)]$ (IV) and $[Cu_2(en)_3(CO)_2](BPh_4)_2$ (V)[5]



$[Cu(en)(CO)(BPh_4)]$ (IV)

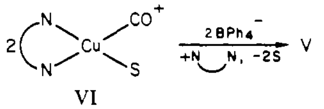


$[Cu_2(en)_3(CO)_2](BPh_4)_2$ (V)

are isolated, depending on the Cu/en molar ratio. The carbonylation of CuI, occurring in the presence of an excess of en, allows the isolation of complex V only.[5] The difference in terms of the complexes isolated in the solid state when en or tmen are used in reactions 2 and 3 is reasonably ascribed to the steric differences between the two amino ligands. Because of the steric hindrance, tmen cannot, probably, display a bridging bonding mode as en in V or allow the phenyl group of a BPh_4^- anion to fill the fourth coordination position around copper(I) in the solid state. This is an interesting result for devising a synthetic strategy for mixed-ligand copper(I) complexes.

As far as the solid state–solution relationship for complexes III is concerned, this is, in fact, a general problem in copper(I)–carbonyl–amine chemistry, and it is the consequence of the very high kinetic lability of copper(I).

It was suggested, mainly on the basis of the IR data, that the existence of binuclear complexes like V must be viewed in the solid state only, since they probably come from a mononuclear solvated species such as VI[5,6] (eq 4).

 (4)

VI

(S = solvent)

We feel that even in the present case, notwithstanding all the CO frequencies both in the solid state and in solution for the species involved in reactions 2 and 3 fall very close, the origin of III can be represented by a reaction like (4).

Table VI. Bond Angles (Deg) in the Cation $[Cu_2(tmen)_2(CO)_2X]^+$

	X		
atoms	Cl	Br	I
Cu(1)-X-Cu(2)	103.0 (1)	102.8 (1)	105.1 (1)
X-Cu(1)-N(1)	104.8 (1)	106.4 (3)	108.2 (3)
X-Cu(1)-N(2)	104.5 (1)	105.9 (2)	108.3 (3)
X-Cu(2)-N(3)	105.6 (1)	106.3 (3)	107.7 (3)
X-Cu(2)-N(4)	107.5 (1)	108.4 (3)	111.7 (3)
X-Cu(1)-C(13)	116.2 (2)	114.7 (4)	111.8 (5)
X-Cu(2)-C(14)	111.0 (2)	109.1 (5)	107.3 (5)
N(1)-Cu(1)-N(2)	87.3 (2)	86.8 (4)	86.6 (4)
N(3)-Cu(2)-N(4)	86.3 (2)	87.4 (4)	86.5 (5)
N(1)-Cu(1)-C(13)	119.2 (2)	119.4 (5)	118.6 (6)
N(2)-Cu(1)-C(13)	120.4 (2)	119.7 (5)	120.6 (6)
N(3)-Cu(2)-C(14)	123.0 (2)	124.0 (6)	125.6 (6)
N(4)-Cu(2)-C(14)	120.4 (2)	119.4 (6)	116.8 (6)
Cu(1)-C(13)-O(13)	179.8 (5)	177.8 (13)	174.3 (14)
Cu(2)-C(14)-O(14)	176.4 (5)	176.0 (13)	174.0 (13)
Cu(1)-N(1)-C(1)	103.9 (3)	105.3 (8)	103.4 (7)
Cu(1)-N(2)-C(2)	102.2 (3)	102.4 (7)	102.8 (8)
N(1)-C(1)-C(2)	111.8 (4)	111.7 (11)	112.6 (10)
N(2)-C(2)-C(1)	111.8 (4)	111.5 (12)	113.6 (11)
C(1)-N(1)-C(5)	109.4 (4)	107.6 (5)	108.3 (10)
C(1)-N(1)-C(6)	111.8 (4)	110.4 (10)	111.1 (10)
C(5)-N(1)-C(6)	108.0 (4)	106.6 (9)	108.8 (10)
C(2)-N(2)-C(7)	107.8 (4)	108.0 (10)	107.1 (10)
C(2)-N(2)-C(8)	112.5 (4)	112.4 (11)	114.0 (10)
C(7)-N(2)-C(8)	107.9 (4)	107.1 (9)	107.9 (9)
Cu(1)-N(1)-C(5)	112.5 (3)	115.7 (8)	116.0 (8)
Cu(1)-N(1)-C(6)	111.8 (3)	111.3 (7)	109.2 (7)
Cu(1)-N(2)-C(7)	115.6 (3)	116.4 (8)	115.1 (8)
Cu(1)-N(2)-C(8)	110.9 (3)	110.5 (7)	110.0 (8)
Cu(2)-N(3)-C(3)	103.8 (4)	103.0 (9)	103.7 (11)
Cu(2)-N(4)-C(4)	103.8 (3)	104.3 (9)	103.3 (10)
N(3)-C(3)-C(4)	112.8 (6)	116.3 (19)	114.4 (19)
N(4)-C(4)-C(3)	112.1 (5)	111.3 (14)	114.9 (15)
C(3)-N(3)-C(9)	111.1 (4)	110.5 (13)	114.3 (13)
C(3)-N(3)-C(10)	109.0 (5)	106.6 (13)	107.8 (15)
C(9)-N(3)-C(10)	107.7 (4)	110.4 (11)	107.1 (12)
C(4)-N(4)-C(11)	114.3 (4)	111.3 (11)	112.3 (12)
C(4)-N(4)-C(12)	107.0 (5)	107.7 (12)	107.6 (14)
C(11)-N(4)-C(12)	106.4 (4)	106.0 (11)	104.8 (13)
Cu(2)-N(3)-C(9)	110.6 (4)	111.3 (8)	108.6 (10)
Cu(2)-N(3)-C(10)	114.7 (3)	114.7 (8)	115.5 (9)
Cu(2)-N(4)-C(11)	113.3 (3)	115.7 (9)	115.7 (9)
Cu(2)-N(4)-C(12)	112.2 (3)	111.7 (8)	113.1 (9)

The nature of the bridging ligand taken up by the two copper(I) in the solid state is mainly imposed by the steric requests of the bidentate amine surrounding the metal. When the hindered amines are involved, the bridging ligand can be the bidentate amine itself, while in reactions 2 and 3 the less crowded halides are preferred. Therefore we feel that the existence of complexes III is probably limited to the solid state only. The structure of III is relevant to (i) the nature of the coordination environment displayed by copper(I) binding carbon monoxide, (ii) the simultaneous presence around copper(I) of a halide ligand and carbon monoxide (the structure of III represents a structural model for the so far undefined "CuCOX" complexes), and (iii) the availability of structural data concerning a complete series of carbonyl complexes of copper(I), bridged by a single halogen.

Description of the Structures. The crystals of complexes III are built up of dinuclear cations $[Cu_2(tmen)_2(CO)_2X]^+$ and BPh_4^- anions, the anion–cation contact interaction being not significantly different and independent of the nature of the halide ligand.

A significant shortening of the nonbonding contacts within the cation is observed from the Cl to Br derivative (Table VII). The same trend, even by a lesser extent, was observed in the iodide complex. This would somewhat explain the trend in

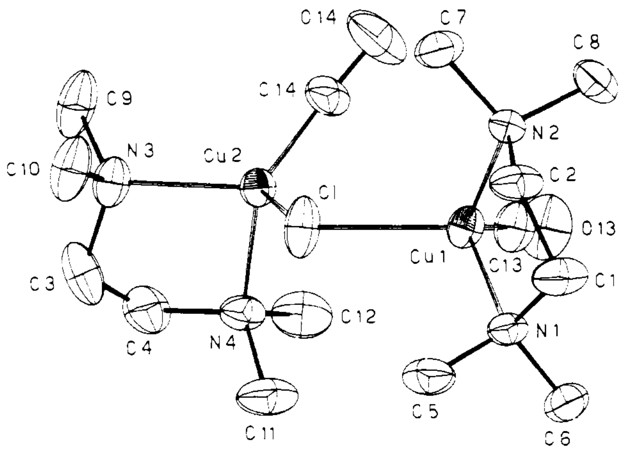


Figure 1. ORTEP[20] drawing of the cation $[Cu_2(tmen)_2(CO)_2Cl]^+$ and atomic numbering scheme of atoms. Hydrogen atoms have been omitted for clarity. Thermal ellipsoids are drawn at the 30% probability level.

Table VII. Nonbonding Contacts (Å) in the Cation $[Cu_2(tmen)_2(CO)_2X]^+$

	X			Δ/σ^a	
atoms	Cl (I)	Br (II)	I (III)	I-II	I-III
Cu(1)· · ·C(1)	2.816 (5)	2.788 (12)	2.802 (12)	2.2	0.3
Cu(1)· · ·C(2)	2.815 (6)	2.800 (14)	2.793 (14)	1.0	1.1
Cu(1)· · ·C(5)	2.967 (5)	2.985 (14)	2.998 (15)	1.2	2.0
Cu(1)· · ·C(6)	2.969 (6)	2.954 (12)	2.931 (14)	1.1	2.5
Cu(1)· · ·C(7)	3.060 (5)	3.037 (14)	3.057 (14)	1.6	0.2
Cu(1)· · ·C(8)	2.975 (7)	2.923 (16)	2.915 (15)	3.0	3.6
Cu(2)· · ·C(3)	2.841 (8)	2.799 (20)	2.817 (21)	1.9	1.1
Cu(2)· · ·C(4)	2.822 (6)	2.827 (16)	2.787 (18)	0.3	1.8
Cu(2)· · ·C(9)	2.977 (6)	2.914 (16)	2.906 (17)	3.7	3.9
Cu(2)· · ·C(10)	3.021 (6)	3.000 (14)	3.016 (18)	1.4	0.3
Cu(2)· · ·C(11)	2.998 (6)	2.957 (17)	3.000 (15)	2.2	0.1
Cu(2)· · ·C(12)	2.993 (7)	2.970 (16)	2.965 (20)	1.3	1.3
O(14)· · ·C(13)	3.611 (7)	3.543 (19)	3.607 (20)	3.4	0.2
O(13)· · ·O(14)	3.631 (7)	3.484 (18)	3.433 (19)	7.6	9.8
O(13)· · ·C(14)	3.643 (7)	3.547 (19)	3.574 (20)	4.7	3.2
N(1)· · ·N(2)	2.895 (4)	2.847 (12)	2.871 (12)	3.8	1.9
N(1)· · ·C(2)	2.454 (6)	2.404 (17)	2.425 (16)	2.8	1.7
N(1)· · ·C(13)	3.338 (6)	3.349 (16)	3.340 (18)	0.6	0.1
N(2)· · ·C(13)	3.387 (6)	3.371 (16)	3.386 (18)	0.9	0.1
N(3)· · ·N(4)	2.876 (6)	2.858 (15)	2.863 (17)	1.1	0.7
N(3)· · ·C(14)	3.397 (6)	3.386 (19)	3.487 (20)	0.5	4.3
N(4)· · ·C(14)	3.353 (5)	3.287 (18)	3.325 (18)	3.5	1.5
C(6)· · ·C(13)	3.513 (8)	3.511 (19)	3.443 (20)	0.2	3.3
C(8)· · ·C(13)	3.574 (9)	3.521 (21)	3.523 (21)	2.3	2.2
C(9)· · ·C(14)	3.605 (8)	3.594 (22)	3.626 (22)	0.5	0.9
C(12)· · ·C(14)	3.553 (8)	3.476 (22)	3.482 (23)	3.3	2.9

[a] $\Delta/\sigma = (x_1 - x_2)/(\sigma_1{}^2 + \sigma_2{}^2)^{1/2}$.

unit cell volumes [X = Cl, 2020.4 (5); X = Br, 2005.2 (5); X = I, 2044 (2) Å^3]. Figure 1 shows a view of the cation. Two copper atoms, with a pseudotetrahedral geometry, are bridged by a halogen atom. In consequence, the X, Cu, C(carbonyl) planes are, practically, orthogonal to the N, Cu, N planes (Tables SX–SXII, available as supplementary material). Greater attention is devoted to the structural data concerning the coordination sphere of the copper atom and the influence of the halogen on the parameters characterizing the overall structure.

The Cu–C and C–O bond distances are practically unaffected by the nature of the halogen, and they compare very well with the values reported for other copper(I)–amine carbonyls.[3-6] A shortening of the copper(I)–N bond distances is observed, in comparison with those found in $[Cu(tmen)(C_6H_{11}NC)_2]^+$[18] (Table V). The N–Cu–N angles have very close values in the dimeric cations (Table VI). The nature of the halogen affects mainly the following parameters. (i) X–Cu–N angles [X = Cl, 105.6 (1); X = Br, 106.5 (2); X = I, 109.0 (2)° (mean values)]: a regular increasing from the Cl to I derivative is observed. (ii) X–Cu–CO angles: a regular decrease is observed (Table VI) with increasing atomic radius. This trend is indicated by the torsional angle, ϕ, C(13)–Cu(1)–Cu(2)–C(14) (Figure 2), diagnostic of the relative arrangement of the two CO ligands in the dimer. The mean value of ϕ decreases (X = Cl, 53.2; X = Br, 50.0; X = I, 46.9°). (iii) Cu(1)···Cu(2): the separation increases with the atomic radius of the halogen (Table V), while the Cu–X–Cu angle is practically constant.

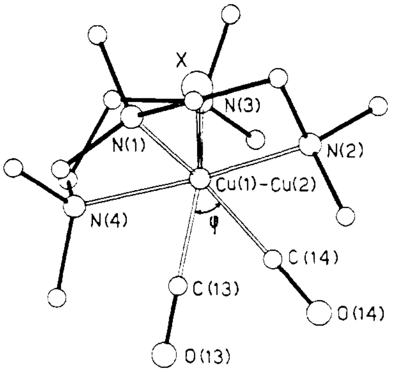


Figure 2. Projection of the cation $[Cu_2(tmen)_2(CO)_2X]^+$ along the Cu···Cu axis (ϕ = 53.2, 50.0, and 46.9° for X = Cl, Br, and I, respectively).

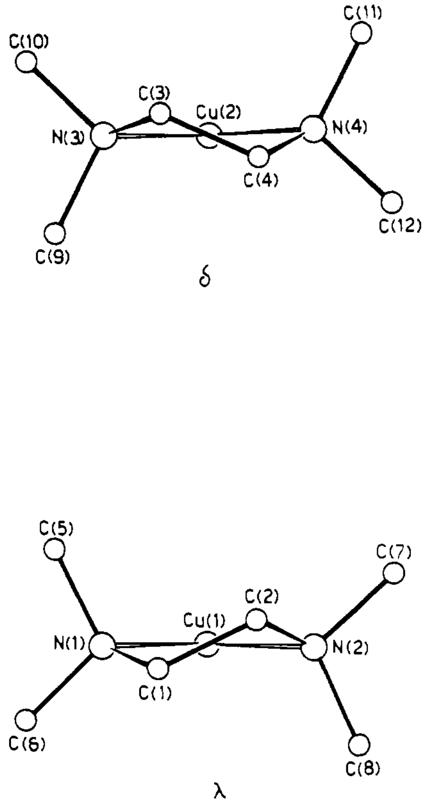


Figure 3. Enantiomeric δ and λ conformations for the two chelate rings present in a dimer. The labeling of the atoms corresponds to the coordinates given in Table II. A dimer enantiomeric with this is present in the structure, generated by a center of symmetry.

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(18) Pasquali, M.; Floriani, C.; Gaetani-Manfredotti, A.; Chiesi-Villa, A. *Inorg. Chem.* **1979**, *18*, 3535.

The monobridging bonding mode of the halogen has no significant influence on the Cu-X bond distances, which agree with those found in mononuclear, singly or doubly bridged copper(I) complexes.[19] Distances and angles within tmen and BPh_4^- units (Tables V and VI and Tables SVII-SIX available as supplementary material) fall in the usual range.[18]

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Registry No. I, 53513-40-9; III, X = Cl, 72840-12-1; III, X = Br, 72840-14-3; III, X = I, 72840-10-9; CuCl, 7758-89-6; CuBr, 7787-70-4; CuI, 7681-65-4; CO, 630-08-0.

Supplementary Material Available: A listing of observed and calculated structure factor amplitudes for all compounds and Tables SI-SIII listing anisotropic thermal parameters, SIV-SVI listing atomic coordinates for hydrogen atoms, SVII-SIX listing distances and angles in BPh_4^- anions, and SX-SXII for least-squares planes (65 pages). Ordering information is given on any current masthead page.

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(19) Baker, E. N.; Garrick, P. M. *J. Chem. Soc., Dalton Trans.* **1978**, 416. Bräuden, C. I. *Acta Chem. Scand.* **1967**, *21*, 1000. Baenziger, N. C.; Richards, G. F.; Doyle, J. R. *Inorg. Chem.* **1964**, *11*, 1529. Gill, J. T.; Mayerle, J. J.; Welcker, P. S.; Lewis, D. F.; Ucko, D. A.; Barton, D. J.; Stowens, D.; Lippard, S. J. *Ibid.* **1976**, *15*, 1155. Churchill, M. R.; Rotella, F. J. *Ibid.* **1979**, *18*, 166 and references cited therein. Jardine, F. H. *Adv. Inorg. Chem. Radiochem.* **1975**, *17*, 115. Churchill, M. R.; Davies, G.; El-Sayed, M. A.; El-Shalzly, M. F.; Hutchinson, J. P.; Rupich, M. W.; Watkins, K. O. *Inorg. Chem.* **1979**, *18*, 2296. Van de Leemput, P. J. H. A. M.; Willemse, J.; Cras, J. A.; Groen, L. *Recl. Trav. Chim. Pays*-Bas **1979**, *98*, 413. Eller, P. G.; Kubas, G. J.; Ryan, R. R. *Inorg. Chem.* **1977**, *16*, 2454.

(20) Johnson, C. K. "ORTEP", Report ORNL-3794; Oak Ridge National Laboratory: Oak Ridge, TN, 1965.

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Crystal Structure and Molecular Geometry of a Trigonal-Bipyramidal Oxo-Alkylidene Complex of Tungsten(VI), $W({=}O)({=}CHCMe_3)(PEt_3)Cl_2$

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The complex $W({=}O)({=}CHCMe_3)(PEt_3)Cl_2$, a catalyst for the metathesis of terminal and internal olefins, crystallizes in the centrosymmetric orthorhombic space group *Pbca* with $a = 9.111$ (2) Å, $b = 15.709$ (4) Å, $c = 24.207$ (6) Å, $V = 3465$ (1) Å^3, and $Z = 8$. Diffraction data ($2\theta = 4.0$–$50.0°$, Mo Kα radiation) were collected on a Syntex $P2_1$ automated four-circle diffractometer, and the structure was solved by conventional methods. All nonhydrogen atoms were located. The tungsten atom lies on a pseudospecial position ($\sim{}^1/_2$, $\sim{}^1/_2$, $\sim{}^1/_8$), and half of the data are systematically weak. Discrepancy indices are $R_F = 0.147$ and $R_{wF} = 0.068$ for all 3055 data and $R_F = 0.073$ and $R_{wF} = 0.055$ for those 1582 data with $|F_o| > 5.0\sigma(F_o)$. The tungsten(VI) atom has a distorted trigonal-bipyramidal coordination geometry with the oxo ligand ($W{=}O = 1.661$ (11) Å), the neopentylidene ligand ($W{=}C(1) = 1.882$ (14) Å), and a chloride ligand ($W{-}Cl(1) = 2.389$ (5) Å) in equatorial sites; the phosphine ligand ($W{-}P = 2.518$ (4) Å and the second chloride ligand ($W{-}Cl(2) = 2.379$ (5) Å) occupy the two axial sites.

Introduction

Although alkylidene derivatives of tantalum and niobium are now well characterized,[1] there are few such complexes known for the other transition metals. Recently, alkylidene *transfer* from tantalum has been shown[2] to yield alkylidene complexes of tungsten (via eq 1).

$$Ta({=}CHCMe_3)(PR_3)_2Cl_3 + W({=}O)(OCMe_3)_4 \rightarrow Ta(OCMe_3)_4Cl + W({=}O)({=}CHCMe_3)(PR_3)_2Cl_2 \quad (1)$$

The resulting products are octahedral oxo-alkylidene complexes of tungsten(VI) and are catalysts for the metathesis of both terminal and internal olefins.[3]

One PR_3 ligand can be removed from the octahedral oxo-alkylidene complexes by adding transition-metal complexes which will scavenge phosphines.[3] (See eq 2.)

$$W({=}O)({=}CHCMe_3)(PR_3)_2Cl_2 + {}^1/_2Pd(PhCN)_2Cl_2 \rightarrow W({=}O)({=}CHCMe_3)(PR_3)Cl_2 + {}^1/_2Pd(PR_3)_2Cl_2 + PhCN \quad (2)$$

We have undertaken a single-crystal X-ray diffraction study of the pentacoordinate complex $W({=}O)({=}CHCMe_3)(PEt_3)Cl_2$, prepared in this manner. A preliminary report has appeared.[3]

We have also attempted to solve the structure of the related octahedral species $W({=}O)({=}CHCMe_3)(PEt_3)_2Cl_2$ but have been frustrated by a severe disorder problem.[4a] Further studies on this class of complexes are being undertaken.[4b]

We now report the details of a structural study on $W({=}O)({=}CHCMe_3)(PEt_3)Cl_2$.

Experimental Section

(A) Collection and Processing of the X-ray Diffraction Data. Yellow, rectangular crystals of $W({=}O)({=}CHCMe_3)(PEt_3)Cl_2$ were provided by Professor R. R. Schrock of the Massachusetts Institute of Technology. The material is slightly air sensitive.

A well-formed crystal of approximate dimensions 0.3 × 0.2 × 0.2 mm was wedged and sealed in a thin-walled glass capillary of appropriate size in an inert-atmosphere drybox. The capillary was then flame sealed, fixed into an aluminum pin with beeswax, and mounted into an eucentric goniometer. Preliminary photographs indicated an orthorhombic unit cell. The crystal was centered on our Syntex $P2_1$ automated diffractometer. Determination of the crystal class, the

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(1) Schrock, R. R. *Acc. Chem. Res.* **1979**, *12*, 98.

(2) Schrock, R. R.; Rocklage, S.; Wengrovius, J. H.; Rupprecht, G. A.; Fellman, J. D. *J. Mol. Catal.* **1980**, *8*, 73.

(3) Wengrovius, J. H.; Schrock, R. R.; Churchill, M. R.; Missert, J. R.; Youngs, W. J. *J. Am. Chem. Soc.* **1980**, *102*, 4515.

(4) (a) This complex crystallizes in the space group *Pbcn* with $Z = 4$ and lies on a crystallographic C_2 axis. The oxo and one chloride ligand are disordered, and there is further rotational disorder of the $CHCMe_3$ and PEt_3 ligands. (b) Since the submission of this article we have succeeded in determining the molecular structure of the related trimethylphosphine complex $W({=}O)({=}CHCMe_3)(PMe_3)_2Cl_2$. See: Churchill, M. R.; Rheingold, A. L.; Youngs, W. J.; Schrock, R. R.; Wengrovius, J. H. *J. Organomet. Chem.* **1981**, *204*, C17-C20.