J|A|C|S
ARTICLES

Gas-Phase Structure of (1,1,1,5,5,5-Hexafluoro-2,4-pentanedionato)(η^2-1,5-cyclooctadiene)copper(I), Cu(1,5-cod)(hfac), an Important Precursor for Vapor Deposition of Copper

Drahomír Hnyk,[†] Michael Bühl,[‡] Paul T. Brain,[§] Heather E. Robertson,[§] and David W. H. Rankin*,[§]

Contribution from the Institute of Inorganic Chemistry, Academy of Sciences of the Czech Republic, CZ- 250 68 Řež near Prague, Czech Republic, Max-Planck-Institut für Kohlenforschung, Kaiser-Wilhelm-Platz 1, D-45470 Mülheim an der Ruhr, Germany, and the Department of Chemistry, University of Edinburgh, West Mains Road, Edinburgh EH9 3JJ, United Kingdom

Received November 8, 2001

Abstract: The molecular structure of Cu(1,5-cod)(hfac) in the gas phase has been determined by electron diffraction, restrained by parameters calculated ab initio (MP2/AE1 level) or using Density Functional Theory (BP86/AE1 level). The most stable structure is one in which one olefinic group of the cyclooctadiene ligand is coordinated to the square-planar copper atom [refined Cu−C distances 194.0(13) and 194.4(9) pm]. The second C═C double bond is weakly associated with the copper atom [Cu···C distances 267.2(23) and 276.9(25) pm], and the cyclooctadiene ligand has a twist-boat conformation, so that the complex has C_1 symmetry. The nature of the bonding between copper and each of the two olefin moieties has been assessed by topological analysis of the BP86/AE1 total electron density. A form with C_2 symmetry, lying between 2 and 7 kJ mol^{-1} above the ground state, is a transition state for exchange of the two olefinic groups. There are also two higher energy conformers, both 10 kJ mol^{-1} or more above the ground state. In one of these the cyclooctadiene ligand retains the twist-boat conformation, but the Cu(hfac) moiety is coordinated in the *exo* position with respect to the noncoordinated olefin, instead of *endo*, as in the most stable conformer. The molecular symmetry is C_1 in this isomer. In the remaining form the ligand has the chair conformation, and the molecular symmetry is C_s.

Introduction

The search for good precursors for chemical vapor deposition of conductors, needed for the production of electronic devices, has focused attention on volatile compounds of appropriate elements. Copper(II) compounds, notably Cu(hfac)2 (hfac = 1,1,1,5,5,5-hexafluoro-2,4-pentanedionato), required quite a high temperature (340−380 °C) for deposition, but copper(I) compounds have proved to be more suitable.[1] Many of these, of the general type Cu(β-diketonate)L, have shown good deposition characteristics, including high volatility, low deposition temperature and high deposition rate, and high purity of the copper film.[2] They decompose on a heated substrate by disproportionation.

$$\mathrm{Cu^{I}(\beta\text{-diketonate})L \rightarrow Cu^{0} + Cu^{II}(\beta\text{-diketonate})_2 + 2L}$$

By appropriate choice of ligands the products other than metallic copper can thus be entirely volatile, and so cause no problems during the deposition process.

Many compounds of this type have been investigated, and those with hfac as the β-diketonate ligand have been particularly valuable. Many different ligands L have been used, and the complex with 1,5-cyclooctadiene was one of the earliest to show potential.[3,4] Although the structure of this compound in the crystalline phase was determined, it is important to know also about the gas-phase structure, which is relevant to the mechanism by which the molecules can interact with the surfaces where decomposition occurs. Cyclooctadiene can act as a bidentate or a monodentate ligand,[5] in the latter case in principle with chair or boat conformations for the ring and *endo* or *exo* arrangements of the ring relative to the metal atom, or it may adopt an intermediate structure. We have therefore determined the structure of Cu(1,5-cod)(hfac) in the gas phase, using the

---

* Corresponding author. E-mail: d.w.h.rankin@ed.ac.uk.

[†] Academy of Science of the Czech Republic.

[‡] Max-Planck-Institut für Kohlenforschung.

[§] University of Edinburgh.

(1) Son, J.-H.; Park, M.-Y.; Rhee, S.-W. *Thin Solid Films* **1998**, *335*, 229.

(2) Shin, H.-K.; Chi, K. M.; Hampden-Smith, M. J.; Kodas, T. T.; Farr, J. D.; Paffett, M. F. *Chem. Mater*. **1992**, *4*, 788.

(3) Chi, K. M.; Shin, H.-K.; Hampden-Smith, M. J.; Duesler, E. N.; Kodas, T. T. *Polyhedron* **1991**, *10*, 2293.

(4) Jain, A.; Chi, K. M.; Hampden-Smith, M. J.; Kodas, T. T.; Farr, J. D.; Paffett, M. F. *J. Mater. Res.* **1991**, *7*, 261.

(5) In the overwhelming majority of complexes with transition metals, cod acts as a bidentate ligand; there are, however, rare examples where cod in its chair form acts as a bridge between two metal fragments. See, for instance: Wurst, K.; Strahle, J. *Z. Anorg. Allg. Chem.* **1990**, *595*, 239.

10.1021/ja012505a CCC: $22.00

Table 1. Experimental Data

camera distance/mm	weighting function/nm^{-1}					correlation parameter	scale factor k^a	electron wavelength/pm^b
	Δs	s_{min}	sw_1	sw_2	s_{max}			
259.56	2	40	60	140	164	0.467	0.973(27)	
199.91	4	48	70	192	224	−0.175	0.931(23)	5.683

[a] Numbers in parentheses are estimated standard deviations of the least significant digits. [b] Determined by reference to the scattering pattern of benzene vapor.

recently developed techniques that make use of both experimental (electron diffraction) and computed data.[6]

Experimental and Computational Section

Electron Diffraction. Electron-scattering intensities for Cu(1,5-cod)(hfac) were recorded on Kodak Electron Image plates using the Edinburgh gas-diffraction apparatus operating at ca. 44.5 kV (electron wavelength ca. 5.7 pm).[7] Nozzle-to-plate distances for the stainless steel inlet nozzle employed were ca. 200 and 260 mm, yielding data in the s range 40−224 nm^{-1}. Three plates for the short and five plates for the long nozzle-to-plate distance were selected for the analysis. The sample and nozzle were held at ca. 408 and 413 K, respectively, during the exposures. The scattering patterns of benzene were also recorded for the purpose of calibration; these were analyzed in exactly the same way as those of Cu(1,5-cod)(hfac) so as to minimize systematic errors in the wavelengths and camera distances. Nozzle-to-plate distances, weighting functions used to set up off-diagonal weight matrix, correlation parameters, final scale factors, and electron wavelengths for the measurements are collected in Table 1. The electron-scattering patterns were converted into digital form by using a computer-controlled Joyce-Loebl MDM6 microdensitometer with a scanning program described elsewhere.[8] The program used for data reduction[8] has been described previously, and the least-squares refinement program, ED96, is a modified version of an established program.[9] The complex scattering factors employed were those listed by Ross et al.[10]

Computational Details. Preliminary geometry optimizations were carried out for the parent Cu(acac)(1,5-cod) (acac = 2,4-pentanedionato) with the Gaussian suite of programs,[11] employing the standard SCF method,[12] the 3-21G basis set on the ligands, and Wachters' all-electron basis[13] on Cu, contracted to (8s5p3d). C_2 symmetry was first imposed, but this was relaxed to C_1 after calculation of the harmonic frequencies revealed two imaginary frequencies. C_2 and C_1 forms were then reoptimized at a gradient-corrected level of density-functional theory, employing Becke's 1988[14] and Perdew's 1986[15] exchange and correlation functionals, a fine integration grid, the standard 6-31G* basis on the ligands, and Wachters' basis on Cu, augmented with two diffuse p and one diffuse d functions.[16] At that level, denoted BP86/AE1, or at comparable ones, geometries of 3d transition-metal compounds are usually described very well.[17] Geometries for the title compound were then optimized at the BP86/AE1 level by using the TURBOMOLE program,[18] employing a medium-sized grid (grid 3).[19] In addition, the most stable C_1 minimum was reoptimized at the RI-MP2 level,[20] i.e., using a very cost-efficient approximation to the conventional MP2 method, together with the appropriate auxiliary basis functions for a fit of charge distributions (uncontracted 13s11p7d6f7g set for Cu, 4s2p1d for H, and 8s5p3d1f for all other atoms).[21] Single-point energy calculations were performed at the conventional MP2/AE1 level with Gaussian94. All MP2 calculations employed the frozen-core approximation. The nature of the form with C_2 symmetry and of the most stable C_1 form was probed by a frequency calculation with Gaussian 98 (after reoptimization with the corresponding quadrature), which revealed only one imaginary frequency for the form with C_2 symmetry, as opposed to two for the parent acac structure. Finally, for the most stable C_1 form a topological analysis of the BP86/AE1 total electron density was performed according to the Atoms-in-Molecules theory,[22] using the Morphy program.[23]

Results and Discussion

Selection of Isomers. Schematic structures of Cu(1,5-cod)(hfac) forms that have been optimized at the BP86/AE1 level are shown as structures **1a**−**d**. The corresponding absolute and relative energies are collected in Table 2, and atomic coordinates are provided in the Supporting Information. Form **1a**, with C_1 symmetry, has the lowest energy at all levels employed and corresponds to the structure found in the solid state (see Table 3 for a comparison).[3] In **1a**, only one olefin moiety of the cod

---

(6) (a) Blake, A. J.; Brain, P. T.; McNab, H.; Miller, J.; Morrison, C. A.; Parsons, S.; Rankin, D. W. H.; Robertson, H. E.; Smart, B. A. *J. Phys. Chem.* **1996**, *100*, 12280. (b) Brain, P. T.; Morrison, C. A.; Parsons, S.; Rankin, D. W. H. *J. Chem. Soc., Dalton Trans.* **1996**, 4589.

(7) Huntley, C. M.; Laurenson, G. S.; Rankin, D. W. H. *J. Chem. Soc., Dalton Trans.* **1980**, 954.

(8) Cradock, S.; Koprowski, J.; Rankin, D. W. H. *J. Mol. Struct.* **1981**, *77*, 113.

(9) ED96, a program for GED data analysis using a PC, was written by N. W. Mitzel, based on an earlier program described in: Boyd, A. S. F.; Laurenson, G. S.; Rankin, D. W. H. *J. Mol. Struct.* **1981**, *71*, 217.

(10) Ross, A. W.; Fink, M.; Hilderbrandt, R. In *International Tables for Crystallography*; Wilson, A. J. C., Ed.; Kluwer Academic Publishers: Dordrecht, The Netherlands, Boston, MA, and London, 1992; Vol. C, p 245.

(11) (a) Frisch, M. J.; Trucks, G. W.; Head-Gorden, M.; Gill, P. M. W.; Wong, M. W.; Foresman, J. B.; Johnson, B. G.; Schlegel, H. B.; Robb, M. A.; Replogle, E. S.; Gomperts, R.; Andres, J. L.; Rahavachari, K.; Binkley, J. S.; Gonzalez, C.; Martin, R. L.; Fox, D. J.; Defrees, D. J.; Baker, J.; Stewart, J. J. P.; Pople, J. A. *Gaussian 92*; Gaussian, Inc.: Pittsburgh, PA, 1992. (b) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. *Gaussian 94*; Gaussian, Inc.: Pittsburgh, PA, 1995. (c) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*; Gaussian, Inc.: Pittsburgh, PA, 1998.

(12) Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; Wiley: New York, 1986.

(13) Wachters, A. J. H. *J. Chem. Phys.* **1970**, *52*, 1033.

(14) Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098.

(15) Perdew, J. P. *Phys. Rev. B* **1986**, *33*, 8822. Perdew, J. P. *Phys. Rev. B* **1986**, *34*, 7406.

(16) Hay, P. J. *J. Chem. Phys.* **1977**, *66*, 4377.

(17) See for instance: (a) Ziegler, T. *Can. J. Chem.* **1995**, *73*, 743. (b) Jonas, V.; Thiel, W. *J. Chem. Phys.* **1995**, *102*, 8474. (c) Bühl, M.; Malkina, O. L.; Malkin, V. G. *Helv. Chim. Acta* **1996**, *79*, 742. (d) Koch, W.; Holthausen, M. C. *A Chemist's Guide to Density Functional Theory*; Wiley-VCH: Weinheim, Germany, 2000, and the extensive bibliography therein.

(18) Ahlrichs, R.; Bär, M.; Häser, M.; Horn, H.; Kölmel, M. *Chem. Phys. Lett.* **1989**, *154*, 165.

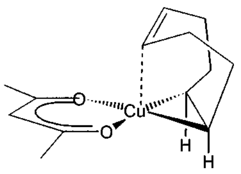
(19) Treutler, O.; Ahlrichs, R. *J. Chem. Phys.* **1995**, *102*, 346.

(20) Weigend, F.; Häser, M. *Theor. Chem. Acc.* **1997**, *97*, 331.

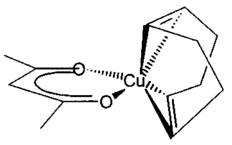
(21) (a) Eichkorn, K.; Weigend, F.; Treutler, O.; Ahlrichs, R. *Theor. Chem. Acc.* **1997**, *97*, 119. (b) Weigend, F. Unpublished results.

(22) (a) Bader, R. F. W. *Atoms in Molecules. A Quantum Theory*; Clarendon Press: Oxford, 1990. (b) Bader, R. F. W. *Chem. Rev.* **1991**, *91*, 893.

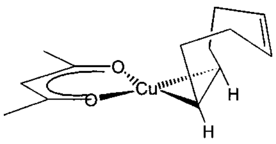
(23) Popelier, P. L. A. *Computer Phys. Commun.* **1996**, *93*, 212.



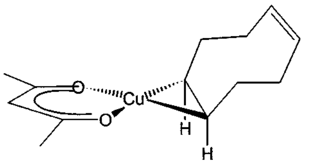
1a (C_1)



1b (C_2)



1c (C_1)



1d (C_s)

group is directly coordinated to the copper center, while the second one appears to be more loosely attached (see the discussion of bonding below).

At the BP86/AE1 level, form **1b**, with C_2 symmetry and two equivalent Cu-olefin interactions, is only slightly higher in energy, 2.3 kJ mol^{-1} (Table 2), but this structure turned out to be the transition state for the migration of the Cu(hfac) unit from one cod double bond to the other, as revealed by second derivative analysis. The MP2/AE1 data in Table 2 indicate a larger energetic separation of **1a** and **1b**, 7.3 kJ mol^{-1}. We have performed MP2 single-point energy calculations, rather than full optimizations for all structures, because the latter are too demanding in computational resources, and only minor changes in the relatives energies are to be expected, and these would not affect the qualitative conclusion we draw from the data. From solid-state ^{13}C CP/MAS NMR spectroscopy, a significantly higher barrier has been estimated for such a process, ca. 60 kJ mol^{-1}.[24] Both the precision of this estimate and the effect of the crystal matrix on the barrier are unknown, however. Our computations for the free molecule predict a very small barrier of 2−7 kJ mol^{-1}.

As noted above, one olefin moiety in **1a** is quite far away from the Cu center (ca. 250−280 pm, Table 3) and appears therefore to be only loosely bound. If the interaction between the Cu atom and this olefin was very weak, isomer **1c** might be comparable in energy and thus present in appreciable amounts in the gas phase. The cod fragments share the same twist-boat conformation in **1a** and **1c**, but the Cu(hfac) moieties are coordinated in *endo* and *exo* positions, respectively, with respect to the noncoordinated olefin. However, **1c** is computed to be significantly higher in energy than **1a**, between 10.4 (BP86) and 26.0 kJ mol^{-1} (MP2). Even with the smaller of these values, the fraction of **1c** in an equilibrium mixture would not exceed 2% at 298 K, or 5% in the gas phase at the nozzle temperature (ca. 413 K) used in the GED experiment.

The same holds for another possible isomer, **1d** (C_s symmetry assumed) with a chair conformation for the cod fragment. For free cod, such a C_s chair form is higher in energy than the C_2 twist-boat by ca. 10 kJ mol^{-1} (BP86/AE1 level) and its presence as a minor component in the gas phase could not be ruled out by GED.[25] The energetic separation between **1a** and **1d** is even larger, between 14.5 (BP86) and 26.7 kJ mol^{-1} (MP2, Table 2), and provides no evidence that **1d** could be present in detectable amounts. If the form **1b** were a potential minimum, it would be populated between ca. 35% and 6% at the temperature of the experiment. Given the tendency of DFT to underestimate reaction barriers, the smaller value, based on the MP2 calculations, is more likely. If, as the calculations suggest, **1b** is a transition structure rather than a minimum, molecular configurations from the transition-state region could contribute to the scattering curve. Such contributions, which would be difficult to incorporate in refinement models for molecules of such dimensions, are probably quite small even in systems with low barriers.[26] The GED model adopted in the refinements is therefore based on the assumption that a single isomer, **1a**, is present, also taking the solid-state structure into account.

Table 2. Absolute (au) and Relative (kJ mol^{-1}, in parentheses) Energies of Optimized (BP86/AE1) and Experimental (H,F-adjusted)[a] Cu(1,5-cod)(hfac) Geometries

structure	BP86		MP2 (single point)	
1a	-2893.49620	(0.0)	-2888.44229	(0.0)
1b	-2893.49531	(2.3)	-2888.43950	(7.3)
1c	-2893.49225	(10.4)	-2888.43239	(26.0)
1d	-2893.49066	(14.5)	-2888.43213	(26.7)
1a (X-ray, 110 K)[a,b]	2893.48617	(26.3)	-2888.43562	(17.5)[c]
1a (X-ray, 296 K)[a,b]	2893.46768	(74.9)	-2888.41751	(65.1)[d]
1a (GED)[a,e]	-2893.47695	(50.5)	-2888.42747	(38.9)[f]

[a] C−H and C−F bond lengths fixed at MP2 values; see text. [b] From ref 18b. [c] 30.9 kJ mol^{-1} relative to the RI-MP2 geometry. [d] 78.4 kJ mol^{-1} relative to the RI-MP2 geometry. [e] Final GED structure, this work. [f] 52.3 kJ mol^{-1} relative to the RI-MP2 geometry.

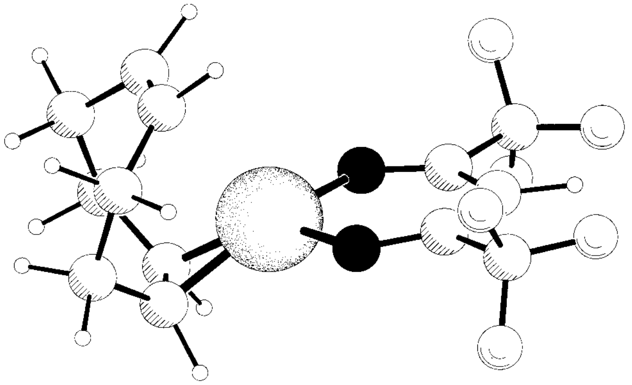


Figure 1. PLUTO plot of a perspective view of the Cu(1,5-cod)(hfac) molecule in the optimum refinement of the electron-diffraction data, also showing the atomic numbering.

Molecular Model and Refinement of the GED Structure. Even with only a single isomer to consider, the title compound constitutes an exceptionally difficult subject for GED. The final structure of this isomer, with the atom numbering scheme, is shown in Figure 1.

The theoretical calculations at both levels showed that there was good reason to assume local symmetry of C_{2v} for the hfac ligand (see Table 3). The corresponding parameters defining the structure of this ligand are listed in the Supporting Information as Table S1.

Modeling of the cod ligand was also based on the results of the theoretical calculations in which a twisted-boat conformation, with very approximately C_2 local symmetry, was found for the

---

(24) Kumar, R.; Fronczek, F. R.; Maverick, A. W.; Kim, A. J.; Butler, L. G. *Chem. Mater.* **1994**, *6*, 587.

(25) Hagen, K.; Hedberg, L.; Hedberg, K. *J. Phys. Chem.* **1982**, *86*, 117.

(26) See for instance the case of B_5H_{11}: even though two degenerate minima are separated by a barrier less than 4 kJ mol^{-1}, refinement of a single conformer proved to be sufficient: Brain, P. T.; Hnyk, D.; Rankin, D. W. H.; Bühl, M.; Schleyer, P. v. R. *Polyhedron* **1994**, *13*, 1453.

Table 3. Selected Geometric Parameters (*r*/pm, angle, deg) for (hfac)Cu(1,5-COD) as Obtained from Different Techniques

parameter	GED[a]	RI-MP2[a]	BP86/AE1[a]	X-ray, 243 K[b]
C(1)═C(2)	142.9(7)	142.1	144.4	136.7(11)
C(5)═C(6)	135.3(19)[c,d]	135.5	135.7	133.1(10)
C(1)−C(8)	151.8(8)	151.3	151.9	150.4(10)
C(4)−C(5)	151.8(8)	151.0	151.7	150.6(12)
C(6)−C(7)	151.8(8)	150.3	151.2	150.3(9)
C(2)−C(3)	153.4(5)	152.2	152.8	152.2(12
C(3)−C(4)	156.5(5)	154.6	155.4	153.6(10)
C(7)−C(8)	156.5(5)	154.3	155.4	152.0(10)
C(12)−C(13)	140.8(7)	140.0[e]	140.9[e]	138.2(10)[e]
C(12)−C(16)	154.9(5)	152.9[e]	154.6[e]	152.2(11)[e]
Cu(9)−C(1)	194.0(13)	196.8	205.5	208.9(7)
Cu(9)−C(2)	194.9(13)	195.9	204.0	204.9(6)
Cu(9)−O(10)	194.4(9)	194.6[e]	197.8[e]	200.0(5)[e]
C(12)−O(10)	128.0(10)	127.4[e]	127.7[e]	124.4(8)[e]
C(15)−F(151)	133.2(3)	135.0[f]	135.8[f]	129.5(10)[f]
Cu(9)···C(5)	267.2(23)[c,d]	255.3	260.9	246.6(8)
Cu(9)···C(6)	276.9(25)[c,d]	269.3	278.2	255.0(7)
C(3)−H(31)	112.4(8)	109.4[f]	110.2[f]	
C(2)−C(1)-C(8)	127.0(5)	127.7	128.7	
C(6)−C(5)-C(4)	129.9(16)[c]	127.9	128.4	
C(1)−C(2)-C(3)	124.9(5)	125.6	126.7	
C(5)−C(6)-C(7)	121.8(17)[c]	125.7	126.7	
C(1)−C(8)-C(7)	118.6(4)	116.2	116.8	
C(3)−C(4)-C(5)	118.6(4)	116.6	116.8	
C(2)−C(3)-C(4)	116.2(4)	114.9	115.1	
C(6)−C(7)-C(8)	116.2(4)	113.1	113.6	
Cu(9)−O(10,11)−C(12,14)	119.5(7)	122.4[e]	121.5[e]	122.5(5)[e]
C(1,2)-Cu(9)−O(10,11)	109.2(5)	110.7[e]	110.9[e,g]	112.0(3)[e,h]
C(3)−C(2)═C(1)−C(8)	1.0[i]	0.7	1.4	
C(4)−C(5)═C(6)−C(7)	2.0(15)[c,d]	1.1	−0.5	
C(2)−C(3)-C(4)−C(5)	40.0(12)	42.6	45.3	
C(1)−C(8)-C(7)−C(6)	43.0(14)	47.2	49.8	
C(1)═C(2)−C(3)−C(4)	−85.1(9)	−86.6	−86.0	
C(5)═C(6)−C(7)−C(8)	−90.2(12)[c]	−92.3	−89.5	
C(2)═C(1)−C(8)−C(7)	36.7(8)	31.5	27.6	
C(3)−C(4)−C(5)═C(6)	36.1(19)[c]	35.6	32.8	

[a] This work. [b] Reference 24. [c] These internal coordinates are not used in the model. [d] Flexibly restrained. [e] C_{2v}-symmetrized values are given. [f] Average values are given. [g] There is a difference between the C(1)−Cu(9)−O(10) and C(2)−Cu(9)−O(11) angles; their values are computed to be 109.4° and 112.4°, respectively. [h] The C(1)−Cu(9)−O(10) and C(2)−Cu(9)−O(11) angles differ quite significantly; their values amount to 108.5(3)° and 115.4(2)°, respectively. [i] Fixed.

ligand (see Table 3). A substantial difference between the lengths of the two double bonds, and small but significant differences between pairs of dihedral angles, which would have been equal if the cod ligand had had exact C_2 symmetry, are the most obvious indications of the breaking of the C_2 symmetry. Restrictions were not placed on these parameters, as some of them would be well-defined by the electron diffraction data, so the difference between the two C═C bond lengths and differences between these pairs of dihedral angles were allowed to vary. The choice of parameters was such that the length of the double bond of the cod ligand not bonded to Cu was a dependent distance.

On the other hand, the differences between the majority of the pairs of C−C single bond lengths and pairs of C−C−C bond angles, each of which would have been identical if the cod ligand had adopted perfect local C_2 symmetry, were minor, comparable to the small deviations from local C_{2v} symmetry in the hfac ligand. In addition, the theoretical calculations prompted us to assume equality of all C−H distances, of all H−C−H angles, all C(sp^3)−C(sp^3)−H angles, and all C(sp^2)−C(sp^2)−H angles. Taking these approximations into account reduced the problem to manageable dimensions. Thus, for example, these simplifications lead to just six different C−C bond distances defining p_1 instead of eleven such distances. Similarly, the four different C(sp^3)−C(sp^3)−C(sp^2) bond angles are approximated by just two angles, of which the average is p_7 and the difference p_{31}.

Possible deviation from perfect planarity of the copper coordination, i.e., of the OOCuCC fragment, was allowed by introduction of the parameter p_{20}, which was defined as folding of the hfac moiety along an axis parallel to the C(1)═C(2) double bond and passing through the Cu atom. By varying p_{21}, which represented rotation of the whole cod ligand about the C(1)═C(2) bond, we could explore possible contact of the second olefinic group [C(5)═C(6)] with Cu. For the sense of these rotations, see Table S1.

In all, 32 independent molecular parameters are needed to define the molecular structure of Cu(1,5-cod)(hfac), as shown in Table S1.

Many geometrical parameters had to be flexibly restrained, as well as some vibrational amplitudes and a few dependent internal coordinates (see Supporting Information, Table S2). This was done by the techniques that we have described as the SARACEN method.[6] Thus, to ensure that the C(5)═C(6) bond length remained in the appropriate region for double bonds, a flexible restraint was imposed on this distance, and to eliminate the proximity effects that contributed quite considerably to the excess energy, the H(31)···H(71) distance within the cod ligand was also flexibly restrained. Similarly, to ensure that the

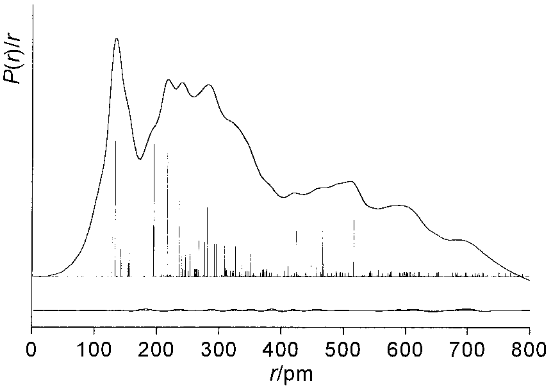


Figure 2. Experimental and difference (experimental − theoretical) radial-distribution curves, $P(r)/r$ against r, for Cu(1,5-cod)(hfac) vapor. Before Fourier inversion, the data were multiplied by $s\ \exp(-0.00002s^2)/(Z_{Cu} - f_{Cu})(Z_F - f_F)$.

H(1) and H(2) atoms were sufficiently bent away from Cu, the Cu···H(1) and Cu···H(2) distances were also subject to flexible restraints. Without these restraints, the Cu−X−C(1,2)−H(1,2) dihedral angles (X is the midpoint of the C(1)═C(2) distance) tended to be smaller (ca. 80°) than the theoretical values (ca. 95°). This discrepancy was also found to contribute to a large extent to the excess energy. Finally, flexible restraints imposed on the two dihedral angles defining the shape of the cod ligand (see Table S2 in the Supporting Information) helped to retain a close approximation to planarity for the olefin which is weakly bound to copper, as in the theoretical structure.

Refinements of the geometrical parameters started with the BP86/AE1 values, and amplitudes of vibration based on those observed or calculated for related compounds. At first the Cu−C(1,2) bond distances remained close to those derived at that level of theory but the Cu−O bond length was shortened quite significantly, approaching the values (r_g) of 191 and 192 pm determined by GED for Cu(acac)$_2$ and Cu(hfac)$_2$ respectively.[27] However, in both these molecules the copper is bivalent, whereas in the compound of the present study it is Cu(I). Consequently, we opted for the RI-MP2/AE1 parameters as the starting values for p_2 and p_3. Since the main difference between these two theoretical structures of **1** is in the lengths of the bonds to copper, subsequent refinements started from the RI-MP2/AE1 values for all the independent molecular parameters. The refined Cu−C(1,2) and Cu−O bond lengths (Table 3) did not depart appreciably from these RI-MP2/AE1 values. However, the peak in the radial-distribution curve (Figure 2) at about 200 pm which arises from these bonds also contains contributions from the six F(151)···F(152) distances, so full resolution of these distances is not possible.

Although many parameters were restrained, no restriction was placed on p_{21}, which defined the extent of interaction of the copper atom with the second C═C double bond. This rotation angle refined to 73.5(9)° from values within the range 65−85°, and values outside the range led to unrealistic geometrical and vibrational parameters. For example, small values of this angle resulted in a long C(5)═C(6) bond (ca. 137 pm) and short C−F bonds (<130 pm, below the lower known limit for these bonds in CF$_3$ groups[28]). On the other hand, movement of the C(5)═C(6) bond to a region that implied bonding with Cu (p_{21} >85°) brought about a considerable shortening of the Cu−O separation (<191 pm). In both of these cases the R factor almost doubled relative to that for the best refinement. The final refinement revealed that just one olefin group was coordinated to the copper atom, with r_a[C(1)═C(2)] = 142.9(7) pm. The compound is therefore a classical olefinic complex with a considerable elongation of the double bond, compared with the uncoordinated C═C bond, for which r_a[C(5)═C(6)] = 135.3(19) pm. This lengthening is typical for a π-complex.[29] For comparison with the theoretical values, see Table 3. Analysis of the computed electron density also indicates a significantly reduced C═C bond order in the coordinated olefin moiety (see below). The stretching frequencies of the coordinated and noncoordinated double bonds are 1517 and 1648 cm^{-1}, respectively (BP86/AE1), in agreement with ref 25. Within the cod ligand some of the dihedral angles are close to those determined by GED for the free ligand;[25] for example, the C(1)C(2)C(3)C(4) angle in the latter refined to −86.5(44)°, compared with −85.1(9)° in the copper complex (Table 3).

The value of p_{20}, which defines the deviation from planarity of the CuC$_2$O$_2$ core of the molecule (see Table S1), was 27.8(16)° in the best refinement, this parameter being refined without any restraint. Forcing a planar arrangement at Cu (p_{20} = 0°) resulted in a short Cu−O bond length (<190 pm) and the R factor was increased considerably.

In addition to the geometrical parameters, 14 amplitudes of vibration were refined. Some of the vibrational parameters for 1,5-cod,[25] Cu(hfac)$_2$,[27] and Cu$_2$(CF$_3$COO)$_2$[30] were taken as starting values. Vibrational amplitudes for groups of similar distances were coupled in blocks and varied under the constraint of constant difference within each block. Interestingly, although the refinable amplitudes of some bonded distances were subjected to flexible restraints, the amplitudes associated with the distances describing the position of the cod ligand relative to Cu refined smoothly. This supports the conclusion that this position is determined reliably from the electron-diffraction data, and is not simply derived from the calculations.

Under these conditions many refinements were carried out, and the various GED models were assessed by single-point energy calculations at the BP86/AE1 level, for comparison with the energy of **1a** fully optimized at that level. Such “excess energies” of refined vs theoretical structures have regularly been used as indicators of possible imperfections of experimental geometries,[31] and the excess energy is used as an additional refinement condition. For the various models considered, the excess energies varied between ca. 60 and 90 kJ mol^{-1}, and

---

(27) Shibata, S.; Sasase, T.; Ohta, M. *J. Mol. Struct.* **1983**, *96*, 347 and references therein.

(28) Oberhammer, H. In *Stereochemical Applications of Gas-Phase Electron Diffraction*; Hargittai, I., Hargittai, M., Eds.; VCH: New York, 1988; Part B, pp 147−207 and references therein.

(29) The C═C bond lengths found in this class of complexes can span the interval 140−147 pm, and the corresponding stretching C═C modes are usually decreased by 140−160 cm^{-1} with respect to a conventional C═C bond. See: Cotton, F. A.; Wilkinson, G.; Murillo, C. A.; Bochmann, M. *Advanced Inorganic Chemistry*, 6th ed.; John Wiley and Sons: New York, 1999; pp 679−681.

(30) Iijima, K.; Ohkawa, J.; Shibata, S. *J. Mol. Struct.* **1987**, *158*, 31.

(31) For recent examples see e.g.: (a) Fox, M. A.; Greatrex, R.; Nikrahi, A.; Brain, P. T.; Picton, M. J.; Rankin, D. W. H.; Robertson, H. E.; Bühl, M.; Li, L.; Beaudet, R. A. *Inorg. Chem.* **1998**, *37*, 216. (b) Brain, P. T.; Bühl, M.; Fox, M. A.; Greatrex, R.; Hnyk, D.; Nikrahi, A.; Rankin, D. W. H.; Robertson, H. E. *J. Mol. Struct.* **1998**, *445*, 319. (c) Hedberg, K.; Hedberg, L.; Bühl, M.; Bethune, D. S.; Brown, C. A.; Johnson, R. D. *J. Am. Chem. Soc.* **1997**, *119*, 5314.

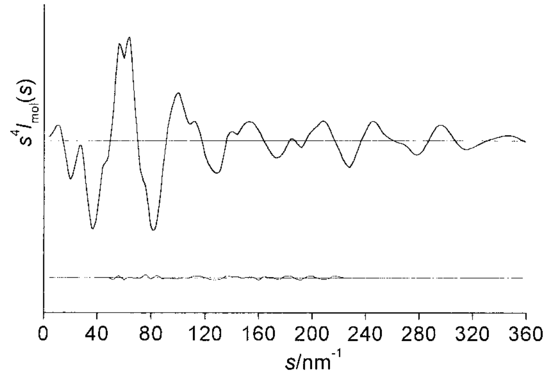


Figure 3. Combined final experimental weighted molecular-scattering intensity curves for Cu(1,5-cod)(hfac).

the R factors were larger than that for the final geometry (see below). To minimize effects due to large vibrational amplitudes associated with the H atoms (a major source of energy differences between experimental r_a and theoretical r_e geometries) and due to possible inadequacies of theoretical bond lengths involving fluorine,[32] the C−H and C−F bond lengths were fixed at their respective mean optimized values[33] in the GED models of lowest energy.

The final GED geometry was chosen on the basis of the lowest H,F-adjusted excess energy, 50.5 kJ mol^{-1} (BP86 level, Table 2). This value is probably acceptable given the size of the system (18 bonded distances in the heavy-atom skeleton). The corresponding excess energy of the low-temperature solid-state geometry at 110 K is considerably lower, 26.3 kJ mol^{-1} (at both BP86 and MP2 levels, Table 2). The difference between these two values probably reflects the increased flexibility at the higher temperature of the GED experiment. The solid-state structure obtained at 296 K performs considerably worse, with an H,F-adjusted excess energy of 74.9 kJ mol^{-1} (BP86 level).

The success of the final refinement, for which the general R factor, R_G, is 0.060 (diagonal R factor (R_D) = 0.059), may be gauged on the basis of the difference between the experimental and calculated radial distribution curves (Figure 2). Figure 3 provides a similar comparison between the experimental and calculated molecular-scattering intensity curves. A perspective view of the molecule in this optimal refinement, the parameters for which are given in Table S1, is shown in Figure 1. The interatomic distances and vibrational amplitudes of the optimal refinement, the most significant elements of the least-squares correlation matrix, and atomic coordinates (BP86/AE1, RI-MP2/AE1, GED) are included in the Supporting Information.

Bonding. The bonding between a transition metal and an olefin is usually interpreted in terms of the Dewar−Chatt−Duncanson (DCD) model[34] based on σ-donation from the olefin to the metal and π-back-donation from the metal to the olefin. A recent topological study of the experimental electron density of Ni(1,5-cod)$_2$ has confirmed this picture:[35] bond paths have been identified from the metal to each of the coordinated olefinic C atoms which are inwardly curved (indicative of σ-donation) but well separated (π back-donation). Essentially the same qualitative result is obtained for Cu(1,5-cod)(hfac) when the coordinated olefin is considered (Figure 4a). Analysis of the BP86/AE1 total electron density clearly reveals two inwardly curved bond paths to copper, i.e., in between the limiting cases of pure σ-donation [as in Cu(C$_2$H$_4$)$^+$ with a T-shaped bond-path pattern][36] and predominant metal-C σ-bonding [as in the metallacycle WCl$_4$(C$_2$H$_4$) with bond paths much closer to linearity].[37,38] The bonding to the coordinated olefin in the title compound is thus fully consistent with the DCD model.

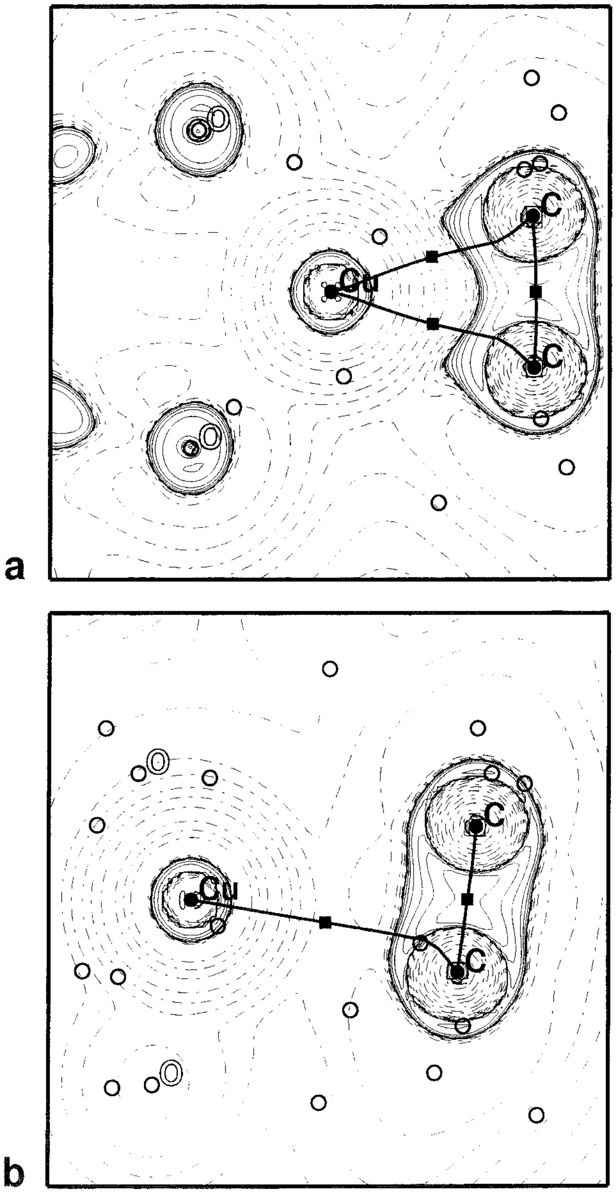


Figure 4. Bond paths and negative Laplacian of the electron density, $-\nabla^2\rho$, in selected planes of **1a** (BP86/AE1 level): (top) plane containing Cu, C(1), C(2); (bottom) plane containing Cu, C(5), C(6) (for atom numbering see Figure 1). Unfilled circles and outlined labels are projections of nuclei into the plot plane. Bold lines are bond paths with critical points marked as filled squares. Solid lines are in regions where electronic charge is concentrated, dashed lines are in regions where charge is depleted.

---

(32) See, for instance: Brain, P. T.; Rankin, D. W. H.; Robertson, H. E.; Fox, M. A.; Greatrex, R.; Nikrahi, A. *Inorg. Chem.* **1997**, *36*, 1048.

(33) Termed "H,F-adjusted" geometries. Frequently, "H-relaxed" or "H,F-relaxed" GED geometries have been used for similar assessments, i.e., with positions of the corresponding atoms optimized and the heavy-atom skeleton fixed to the experimental geometry. This was not done in the present study because of the large computational expense involved.

(34) (a) Dewar, J. S.; *Bull. Soc. Chim. Fr.* **1951**, *18*, C71. (b) Chatt, J.; Duncanson, L. A. *J. Chem. Soc.* **1953**, 2939.

(35) Macchi, P.; Proserpio, D. M.; Sironi, A. *J. Am. Chem. Soc.* **1998**, *120*, 1447.

(36) Böhme, M.; Wagener, T.; Frenking, G. *J. Organomet. Chem.* **1996**, *520*, 31.

(37) Frenking, G.; Pidun, U. *J. Chem. Soc., Dalton Trans.* **1997**, 1653.

The bonding to the second, more distant olefin is qualitatively different. Topological analysis reveals only a single bond path between the copper center and one of the olefinic carbon atoms (Figure 4b). The charge distribution in this olefinic moiety, as visualized by the Laplacian of ρ, is almost undisturbed by the metal, in contrast to the situation involving the coordinated olefin, where a significant charge concentration between the Cu and both olefinic C atoms is revealed (Figure 4a).

Interestingly, the bond-path pattern in Figure 4b is reminiscent of that in a "X−H⋯π hydrogen bond",[39] for instance in an FH⋯fluoroacetylene complex.[40,41] Interaction energies of complexes of HF and π-systems have been computed in the 16−23 kJ mol^{-1} range[40] (MP2 or B3LYP level).[42] The corresponding bond strength between Cu and the distant olefin in Cu(1,5-cod)(hfac), as estimated from the energetic separation between **1a** and **1c**, is in a similar range, ca. 10−26 kJ mol^{-1} (MP2 and BP86 levels, respectively, see Table 2).[43] The two bonding modes may thus be related.

The bond dissociation energy, D_e, of **1a**, forming free cod and Cu(hfac), amounts to 178.1 kJ mol^{-1} at the BP86/AE1 level. The corresponding D_e of **1c**, an estimate of the bond strength of the coordinated olefin, is thus 167.7 kJ mol^{-1},[44] i.e. somewhat smaller than D_e of $Cu(C_2H_4)^+$, 183.7 kJ mol^{-1} [CCSD(T) level].[28]

In summary, topological analysis of the total electron density confirms the fundamentally different bonding of the two cod olefin groups to copper: one is firmly bound via the classical donor−acceptor interaction of the DCD model, while the other is only loosely attached in a manner similar to the bonding in X−H⋯π interactions. The way is then open, with only a small energy cost, to arrangement so that the second olefin group becomes orientated in a way that will allow coordination to a second metal atom. By such a mechanism the disproportionation of the compound could commence.

Acknowledgment. We thank Prof. M. J. Hampden-Smith (formerly of the University of New Mexico) for the sample of Cu(1,5-cod)(hfac). M.B. thanks Prof. W. Thiel for his continuous support and the Fonds der chemischen Industrie for a Liebig fellowship. Assistance of Prof. P. L. A. Popelier and F. Weigend with the Morphy and TURBOMOLE programs, respectively, is gratefully acknowledged. Calculations were performed on Silicon Graphics PowerChallenges (Organisch-chemisches Institut, Universität Zürich), on IBM RS6000 workstations (C4 cluster, ETH Zürich), on NEC-SX3 and SX4 supercomputers (CSCS, Manno, Switzerland), and on Compaq XP1000 and ES40 workstations at the Max-Planck-Institut Mülheim. D.H. acknowledges the Ministry of Education of the Czech Republic (Project LN00A028) and the University of Edinburgh for financial support.

Supporting Information Available: Details of the definitions of refinable parameters, flexible restraints used in the SARACEN refinement of the gas-phase structure of Cu(1,5-cod)(hfac), interatomic distances and amplitudes of vibration, the least-squares correlation matrix for this refinement, and atomic coordinates for computed and experimental structures (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

JA012505A

---

(38) The metallacycle also has very similar M−C and C−C bond orders. The bond orders n can be estimated from the density ρ_{bcp} at the bond critical points according to the equation $n = \exp[A(\rho_{bcp} - B)]$, where A and B are fitted to yield $n = 1$ and 2 from the ρ_{bcp} values of ethane and ethylene, respectively, computed at the same level, cf. ref 22 (BP86/AE1: $A = 7.073$ au, $B = 0.237$ au). Very different bond orders are obtained for the Cu−C and C=C bonds in Cu(1,5-cod)(hfac), 0.34 and 1.56, respectively, indicating that no metallacycle is present. Note also the reduced bond order in the coordinated olefin moiety compared to that in the uncoordinated one, 1.90.

(39) E.g.: Steiner, T. *J. Chem. Soc., Chem. Commun.* **1995**, 95.

(40) Rozas, I.; Alkorta, I.; Elguero, J. *J. Chem. Phys. A* **1997**, *101*, 9457.

(41) Perfectly symmetrical X−H⋯π bonds as in FH⋯acetylene or FH⋯ethylene (both C_{2v} symmetry) are characterized by "conflict catastrophe structures" (cf. ref 22), i.e., a bond path between the H atom and the midpoint of the CC bond (ref 40). A slight perturbation of the symmetry changes the molecular graph dramatically, resulting in a "normal" bond path between the H atom and one of the C atoms.

(42) Without corrections for basis-set superposition error (BSSE); inclusion of BSSE corrections reduces the values to ca. 12−18 kJ mol^{-1}, cf. ref 36.

(43) In addition, the bond order between Cu and the distant olefinic C atom in Cu(1,5-cod)(hfac), 0.23 (as derived by the procedure detailed in footnote 38), is very similar to that between H and the C=C bond in the FH⋯ethylene complex, 0.25 (as obtained from the B3LYP data of ref 40).

(44) An experimental estimate has been given for the activation energy for cod dissociation from a Cu(100) surface, 59 kJ mol^{-1}, based on temperature-programmed desorption (Dubois, L. H.; Zegarski, B. R. *J. Electrochem. Soc.* **1992**, 139, 3295); a bonding situation very different from that in Cu(1,5-cod)(hfac) clearly prevails in this case.