Inorg. Chem. **1997,** *36,* 2505−2510

Structural Flexibility of the Hydrogen-Free Acceptor Ligand Octachloro-1,10-phenanthroline in Its Complexes with d^{10} Metal Ions

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Received July 17, 1996⊗

A remarkable pattern of structural diversity has been observed for the conformation of octachloro-1,10-phenanthroline (ocp) in its free form and in its d^{10} metal complexes $[M(ocp)_2]^+$, M = Cu, Ag, and $Cl_2Hg(ocp)$. Ocp: $C_{12}Cl_8N_2$, monoclinic, space group $P2_1/c$, $a = 5.6390(10)$ Å, $b = 24.970(3)$ Å, $c = 10.4660(10)$ Å, $\beta = 101.33°$, $Z = 4$; $[Ag(ocp)_2](PF_6)\cdot CH_2Cl_2$, $C_{25}H_2AgCl_{18}F_6N_4P$, monoclinic, space group $P2/n$, $a = 13.185(2)$ Å, $b = 9.4740(10)$ Å, $c = 16.106(2)$ Å, $\beta = 92.05°$, $Z = 2$; $Cl_2Hg(ocp)\cdot 2.5C_6H_6$: $C_{27}H_{15}Cl_{10}HgN_2$, triclinic, space group $P\bar{1}$, $a = 10.391(2)$ Å, $b = 12.911(3)$ Å, $c = 13.647(3)$ Å, $\alpha = 103.53(3)°$, $\beta = 111.85(3)°$, $\gamma = 103.69(3)°$, $Z = 2$. While ocp is virtually planar in the previously characterized ion $[Cu(ocp)_2]^+$, the analogous silver(I) complex contains slightly twisted ocp ligands. In contrast, both the free, noncoordinated ligand and its dichloromercury(II) complex exhibit distincly saddle-shaped ocp. $Cl_2Hg(ocp)$ in particular contains a rather distorted chelate ligand. *Ab initio* calculations at the 6-31G** level show a flat energy hypersurface for ocp with an absolute minimum at a saddle-shaped conformation and a second energy minimum, 2.7 kcal/mol higher, for the coplanar arrangement. Nonbonded interactions between the chlorine atoms are responsible for the structural flexibility and limited coordination ability of ocp; electronically, ocp is a good acceptor ligand with two stabilized and close-lying unoccupied π^* orbitals but much reduced σ donor capacity.

Introduction

Metal complexes containing 1,10-phenanthroline ligands have received wide attention because of their long-standing application in analytical chemistry.[1] Copper complexes in particular have found more recent uses as “chemical nucleases” for site-specific DNA cleavage[2] and as photoactivated catalysts.[3] The structures of such molecules are also of relevance for molecular recognition and supramolecular chemistry, e.g., for the synthesis of catenates and knotted molecules,[4] for photophysical studies,[3b,5] for an understanding of the coordination and functioning of copper centers in proteins,[6] and for potential pharmaceutical uses.[7]

In view of these possible applications there were several efforts reported to tune the physical and chemical properties of the 1,10-phenanthroline π system through chemical modification.[8,9] 1,10-Phenanthrolines behave as σ (chelate) donor/π acceptor ligands, which implies that the low-lying π^* orbitals are an attractive target for modifying the electrochemical or excited state properties of corresponding complexes. Recent experimental and theoretical studies have outlined the possibility of having either the $a_2(\chi)$ or $b_1(\psi)$ π MO as the lowest-lying orbital, depending on the substituent pattern of 1,10-phenanthroline;[9] EPR/ENDOR spectroscopy of the ligand-reduced[6a,9−11] forms is well suited to distinguish between both alternatives[9,10] (Chart 1).

⊗ Abstract published in *Advance ACS Abstracts,* May 15, 1997.

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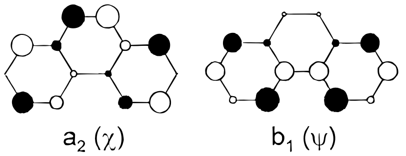
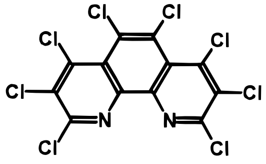
S0020-1669(96)00837-3 CCC: $14.00

Chart 1



In another such attempt at modification we recently presented a first systematic study directed at the coordination behavior of the perchlorinated derivatives of the common α-diimine chelate ligands 2,2′-bipyridine and 1,10-phenanthroline.[12] Octachloro-1,10-phenanthroline (ocp), which was obtained via chlorination with PCl_5 under pressure, failed to form stable complexes with many common transition metal ions such as Fe^{2+}, Mn^{2+}, Ru^{2+}, Ni^{2+}, Zn^{2+}, and Cd^{2+} but yielded complex cations $[M(ocp)_2]^+$ with M = Cu and Ag. The crystal structure analysis of the red tetrafluoroborate of the copper(I) complex revealed a distorted tetrahedral coordination, two virtually planar ocp ligands intersecting at almost a right angle. In contrast to ocp, octachloro-2,2′-bipyridine showed no detectable complexation with Cu^+ or other metal ions, most probably due to its inability to exhibit a low-energy *cis*-coplanar conformation.[12]



ocp

Perchlorination is expected to increase the acceptor capability of organic π systems, as is known, e.g., from the *p*-quinone/tetrachloro-*p*-quinone (chloranil) pair.[13] New acceptor ligands are sought after materials, especially when hydrogen-free such as the nonchelate example TCNE.[14] On the other hand, transition metal complexes with perhalogenated ligands have been much investigated as potential oxidation catalysts.[15] Among the reasons is the higher activation of C−Hal vs C−H bonds toward dissociation in highly oxidized intermediates, Hal^+ ions being much poorer leaving groups than H^+. Additionally, C−H bonds are more readily attacked by $RO^\bullet$ intermediates. Examples include especially macrocyclic ligands such as the porphyrins;[15] small perchlorinated aromatic ligands were also studied to investigate unusual and normally very reactive oxidation states such as Pt(III).[16] Despite this well-known approach, the perhalogenated derivatives of the standard α-diimine chelate ligands 2,2′-bipyridine or 1,10-phenanthroline had not yet been systematically studied prior to our recent work[12] although the parent compounds and their organosubstituted derivative ligands were employed in arrangements for oxidation catalysis.[17] Interest in perchlorinated aromatics and their reactivity is also fostered by attempts to understand their behavior in the environment, i.e., their oxidative or hydrolytic degradation (or lack thereof) by enzymes such as cytochrome P-450.[18]

In this contribution we now describe the crystal structures of the d^{10} metal compounds $[Ag(ocp)_2](PF_6)\cdot CH_2Cl_2$ and $Cl_2Hg(ocp)\cdot 2.5C_6H_6$ and of the metal-free ligand. The results will be compared with those of the copper(I) compound $[Cu(ocp)_2](BF_4)$ reported recently,[12] and the remarkable structural variety will be assessed using *ab initio* calculations of ocp at the 6-31G** level. Similar basis sets have been used recently in calculations of polychlorinated aromatic hydrocarbon molecules.[19]

Experimental Section

Materials. Octachloro-1,10-phenanthroline (ocp) and $[Ag(ocp)_2](PF_6)$ were synthesized as described previously.[12]

Dichloro(octachloro-1,10-phenanthroline)mercury(II) ($Cl_2Hg(ocp)$). A solution of 200 mg (0.439 mmol) of ocp in 25 mL of benzene was added to 119 mg (0.439 mmol) of $HgCl_2$, dissolved in 25 mL of benzene. The clear solution was stirred for 4 h at reflux temperature. After removal of most of the solvent the concentrated solution was kept at 4 °C for 3 days, whereupon colorless crystals of $[Cl_2Hg(ocp)]\cdot 2.5C_6H_6$ suitable for X-ray analysis separated in 82% yield (262 mg). Mp: 222 °C. ^{13}C NMR (C_6D_6): δ 125.2 (C(3)), 130.7 (C(5)), 133.8 (C(4a)), 140.2 (C(4)), 142.3 (C(10a)), 150.4 (C(2)). Anal. Calcd for $C_{12}Cl_{10}HgN_2$ (727.24): C, 19.82; N, 3.85. Found: C, 19.89; N, 3.73.

Instrumentation. ^{13}C NMR spectra were taken on a Bruker AC 250 spectrometer.

X-ray Crystallography. Colorless single crystals of ocp were obtained by slow diffusion of acetone into a benzene solution of ocp, light-yellow crystals of $[Ag(ocp)_2](PF_6)\cdot CH_2Cl_2$ were grown by cooling to 4 °C of a solution in 1/1 dichloromethane/methanol (v/v), and colorless single crystals of $Cl_2Hg(ocp)\cdot 2.5C_6H_6$ were obtained as described above from the reaction solution in benzene. All measurements were made with graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å) on a Syntex P4 (ocp ligand, silver complex) or Syntex $P2_1$ diffractometer (mercury complex). Information on crystal data, intensity collection, and structure refinement are summarized in Table 1. An empirical absorption correction (ψ scans) was applied for the heavy metal complexes.[20] The extinction parameter x was refined by least-squares methods for the mercury(II) complex where F_c was multiplied by the expression

$$k[1 + 0.001xF_c^2\lambda^3/\sin(2q)]^{-1/4}$$

k being the overall scale factor.[20] The structures were solved via direct methods using the SHELXTL-PLUS program package.[21a] Refinement was carried out using SHELXL93,[21b] employing full-matrix least-squares methods for F^2. All non-hydrogen atoms were refined anisotropically, except for those in one of the solvent molecules (C(21)−C(26)) of $Cl_2Hg(ocp)\cdot 2.5C_6H_6$. That particular benzene molecule showed disorder and half-occupancy. The hydrogen atoms were placed in their ideal positions and were allowed to ride on the corresponding carbon atoms.

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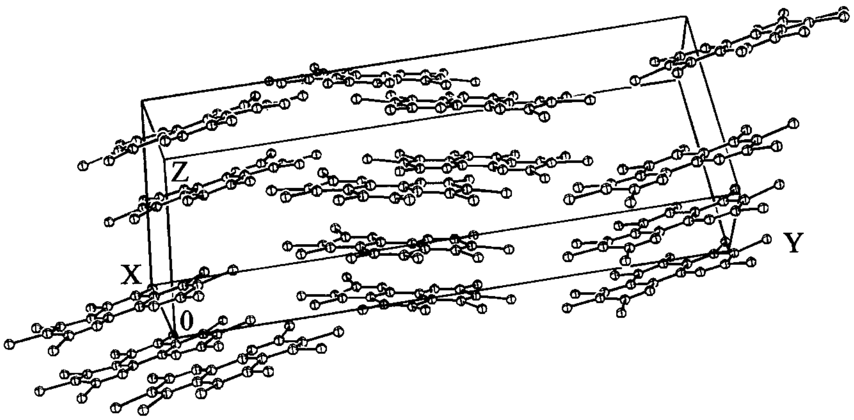

Figure 1. Packing of ocp molecules in the crystal.

Table 1. Crystallographic Data

	ocp	$[Ag(ocp)_2](PF_6)\cdot CH_2Cl_2$	$Cl_2Hg(ocp)\cdot 2.5C_6H_6$
formula	$C_{12}Cl_8N_2$	$C_{25}H_2Ag_1Cl_{18}F_6N_4P_1$	$C_{27}H_{15}Cl_{10}Hg_1N_2$
fw	455.74	1249.25	922.5
space group	$P2_1/c$	$P2/n$	$P\bar{1}$
a, Å	5.6390(10)	13.185(2)	10.391(2)
b, Å	24.970(3)	9.4740(10)	12.911(3)
c, Å	10.4660(10)	16.106(2)	13.647(3)
α, deg	90	90	103.53(3)
β, deg	101.33	92.05	111.85(3)
γ, deg	90	90	103.69(3)
V, Å^3	1445.0(3)	2010.6(4)	1542.2(6)
Z	4	2	2
T, °C	−85	−85	−85
λ, Å	0.710 73	0.710 73	0.710 73
ρ_{calcd}, g·cm^{-3}	2.095	2.063	1.987
μ(Mo Kα), cm^{-1}	15.51	16.59	29.42
R, R_w	0.0451, 0.1507	0.0529, 0.1405	0.0343, 0.0915

[a] $R = (\sum||F_o| - |F_c||)/\sum|F_o|$. [b] $R_w = \{\sum[w(|F_o|^2 - |F_c|^2)^2]/\sum[w(F_o^4)]\}^{1/2}$. [c] GOF $= \{\sum w(|F_o|^2 - |F_c|^2)^2/(n - m)\}^{1/2}$; n = number of reflections; m = number of parameters.

***Ab Initio* Calculations.** Calculations were performed using the GAUSSIAN94 program package.[22] The geometry of ocp was optimized at the 6-31G** level, a basis set[22b] that was similarly used for the calculation of polychlorinated carbocyclic compounds.[19]

Results

Molecular and Crystal Structures. Crystallographic data for the three new structures are listed in Table 1.

The packing of the slightly saddle-shaped ocp molecules in the crystal is illustrated in Figure 1. Figure 2 shows the molecular structure of one individual molecule with the atomic numbering. Selected bond distances and angles are summarized in Table 2; characteristic torsional angles for all ocp systems and nonbonded Cl- -Cl distances for the noncoordinated ocp ligand are listed together with calculated structural data in Tables 5 and 6 (below).

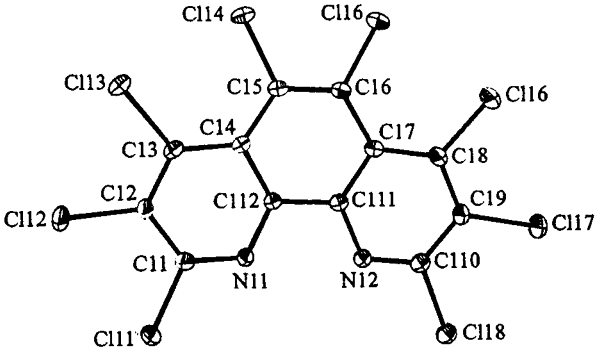

Figure 2. Molecular structure of ocp in the crystal with atomic numbering (ORTEP plot, 50% probability ellipsoids).

Table 2. Selected Bond Lengths (Å) and Angles (deg) for Ocp

Bond Lengths			
Cl(11)−C(11)	1.722(3)	C(11)−C(12)	1.406(4)
Cl(12)−C(12)	1.712(3)	C(12)−C(13)	1.382(5)
Cl(13)−C(13)	1.722(3)	C(13)−C(14)	1.432(5)
Cl(14)−C(15)	1.724(3)	C(14)−C(15)	1.445(4)
Cl(15)−C(16)	1.725(3)	C(15)−C(16)	1.373(5)
Cl(16)−C(18)	1.711(4)	C(16)−C(17)	1.449(4)
Cl(17)−C(19)	1.715(3)	C(17)−C(18)	1.431(5)
Cl(18)−C(110)	1.733(3)	C(18)−C(19)	1.392(5)
N(11)−C(11)	1.306(4)	C(19)−C(110)	1.403(5)
N(11)−C(112)	1.350(4)	C(14)−C(112)	1.418(4)
N(12)−C(110)	1.298(4)	C(17)−C(111)	1.407(4)
N(12)−C(111)	1.355(4)	C(111)−C(112)	1.456(4)
Bond Angles			
av bond angles involving C, N, or Cl	119.9		
min: N(11)−C(112)−C(111)	114.8(3)		
max: C(13)−C(14)−C(15)	128.4(3)		

The molecular structure of a unit $[Ag(ocp)_2](PF_6)\cdot CH_2Cl_2$ in the crystal is depicted in Figure 3, revealing the slightly twisted form of the ocp ligand. The dihedral angle between the planes Ag(1)/N(11)/N(12) and Ag(1)/N(11a)/N(12a) is 70.5°, deviating significantly[4e,f] from the 90° required for close to tetrahedral arrangement. Selected bond lengths and angles are summarized in Table 3.

The solvated structure of $Cl_2Hg(ocp)\cdot 2.5C_6H_6$ is shown in Figure 4. One of the benzene molecules (C(21)−C(26)) is disordered with only half-occupancy; selected bond lengths and angles are listed in Table 4. Of the nondisordered benzene molecules the closest contact made to $Cl_2Hg(ocp)$ is via C(110)- -C(43) (3.33 Å).

***Ab Initio* Calculations of Ocp.** Geometry optimization without symmetry constraints at the 6-31G** level yielded as the energy minimum a saddle-shaped arrangement as depicted schematically in Figure 5. Since the pyridine rings within calculated ocp deviate slightly from planarity, there is no convenient way to model the energy hypersurface with only two parameters. The structure has approximate C_s symmetry,

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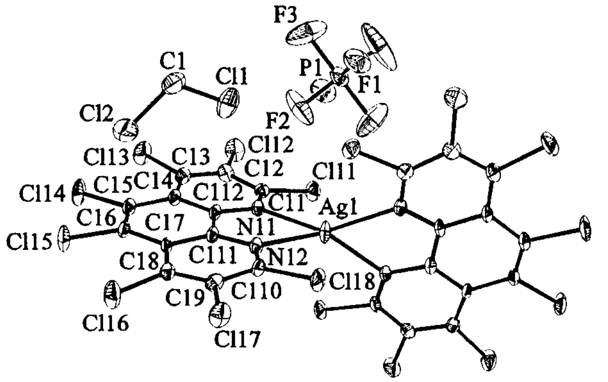


Figure 3. Molecular structure of $[Ag(ocp)_2](PF_6)\cdot CH_2Cl_2$ in the crystal with atomic numbering (ORTEP plot, 50% probability ellipsoids).

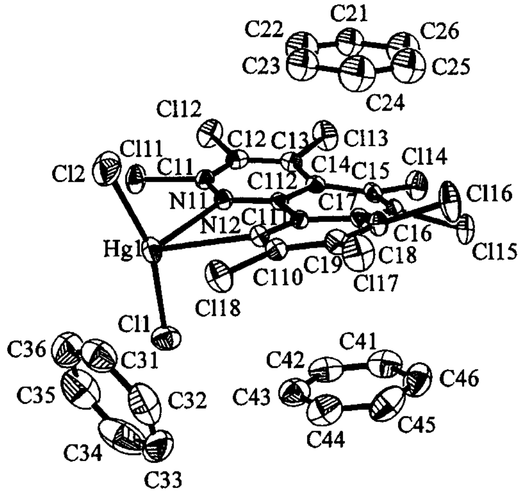


Figure 4. Molecular structure of $Cl_2Hg(ocp)\cdot 2.5C_6H_6$ in the crystal with atomic numbering (ORTEP plot, 50% probability ellipsoids except for the upper disordered benzene molecule, for which only one orientation is depicted).

Table 3. Selected Bond Lengths (Å) and Angles (deg) for $[Ag(ocp)_2](PF_6)\cdot CH_2Cl_2$

Bond Lengths			
Ag(1)−N(11)	2.345(3)	Cl(16)−C(18)	1.716(4)
Ag(1)−N(12)	2.349(3)	Cl(17)−C(19)	1.706(4)
Cl(11)−C(11)	1.710(4)	Cl(18)−C(110)	1.714(4)
Cl(12)−C(12)	1.704(4)	N(11)−C(11)	1.296(5)
Cl(13)−C(13)	1.715(4)	N(11)−C(112)	1.359(5)
Cl(14)−C(15)	1.717(4)	N(12)−C(110)	1.304(5)
Cl(15)−C(16)	1.728(4)	N(12)−C(111)	1.355(4)

av C−C	1.414
min C−C: C(15)−C(16)	1.355(6)
max C−C: C(14)−C(15)	1.454(5)

Bond Angles			
N(11)−Ag(1)−N(12)	68.22(11)	C(11)−N(11)−Ag(1)	120.2(2)
N(11)#−Ag(1)−N(11)[a]	144.6(2)	C(112)−N(11)−Ag(1)	119.9(2)
N(11)−Ag(1)−N(12)#	125.40(10)	C(110)−N(12)−Ag(1)	120.0(2)
N(12)#−Ag(1)−N(12)	139.9(2)	C(111)−N(12)−Ag(1)	119.8(2)

av bond angles involving C, N, or Cl	120.0
min: C(19)−C(18)−C(16)	115.3(3)
max: C(18)−C(17)−C(16)	128.1(3)

[a] #: atoms in centrosymmetric position.

and the calculated bond lengths (Table 5) are within 0.013 Å of the experimental values (Table 2). Selected torsional angles are listed in Table 6 together with corresponding experimental values.

For ocp constrained to a planar structure a local energy minimum has been found, lying 2.7 kcal/mol above the absolute energy minimum (saddle shape, Figure 5). Small deviations from planarity yield slightly higher total energies supporting the notion of a local energy minimum. Overall, however, the energy hypersurface around both calculated and observed minimum structures is rather flat, as indicated by additional *ab initio* calcalutions done for ocp as it occurs in $[M(ocp)_2]^+$ cations (M = Cu[12] and M = Ag: Figure 3, Table 3). The twisted structure of ocp from the silver compound lies only 0.4 kcal/mol higher than the absolute minimum whereas the close to planar structure of ocp in the copper(I) complex lies 3.2 kcal/mol higher, i.e., still slightly higher than the completely planar form.

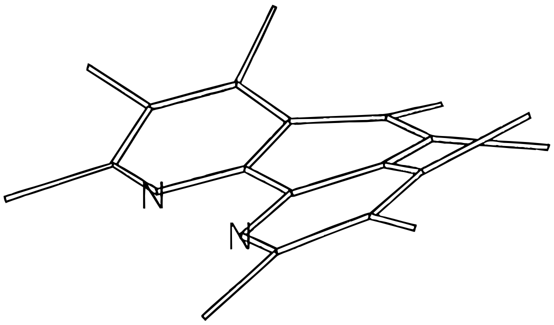


Figure 5. Calculated energy minimum structure of ocp (*ab initio*, 6-31G** basis).

Table 4. Selected Bond Lengths (Å) and Angles (deg) for $Cl_2Hg(ocp)\cdot 2.5\ C_6H_6$

Bond Lengths			
Hg(1)−Cl(1)	2.302(2)	Cl(15)−C(16)	1.723(4)
Hg(1)−Cl(2)	2.292(2)	Cl(16)−C(18)	1.714(4)
Hg(1)−N(11)	2.629(3)	Cl(17)−C(19)	1.710(4)
Hg(1)−N(12)	2.586(3)	Cl(18)−C(110)	1.715(4)
Cl(11)−C(11)	1.721(4)	N(11)−C(11)	1.305(5)
Cl(12)−C(12)	1.702(4)	N(11)−C(112)	1.349(5)
Cl(13)−C(13)	1.708(4)	N(12)−C(110)	1.309(5)
Cl(14)−C(15)	1.717(4)	N(12)−C(111)	1.350(5)

av C−C	1.411
min C−C: C(15)−C(16)	1.371(6)
max C−C: C(14)−C(15)	1.451(5)

Bond Angles			
Cl(1)−Hg(1)−N(11)	94.73(9)	Cl(2)−Hg(1)−N(12)	99.46(9)
Cl(1)−Hg(1)−N(12)	96.18(9)	Cl(2)−Hg(1)−Cl(1)	162.19(6)
Cl(2)−Hg(1)−N(11)	100.23(10)	N(12)−Hg(1)−N(11)	61.19(10)

av bond angles involving C, N, or Cl	119.9
min: N(11)−C(112)−C(111)	115.3(3)
max: C(13)−C(14)−C(15)	127.5(4)

Table 5. *Ab Initio* Calculated Bond Lengths (Å) for Ocp (C_s Symmetry)

N(11)−C(11)	1.286	N(11)−C(112)	1.333
C(112)−C(14)	1.394	C(11)−C(12)	1.412
C(12)−C(13)	1.375	C(13)−C(14)	1.423
C(14)−C(15)	1.460	C(15)−C(16)	1.349
C(111)−C(112)	1.459		
C−Cl (av)	1.724		

In view of our previous efforts to elucidate the nature of π^* orbital ordering in 1,10-phenanthroline and its derivatives,[9] we also studied the ocp molecule in that respect. For all geometries considered we calculated two very close-lying unoccupied π^* orbitals of the χ and ψ types (Chart 1), the separation being less than 0.03 eV. Whereas the χ MO is slightly lower for the planar arrangement, this situation is reversed for the fully optimized saddle-shaped situation. Generally, these π^* MOs are strongly stabilized in ocp relative to unsubstituted 1,10-phenanthroline; using the same 6-31G** basis set this stabilization due to the substitution by eight chlorine atoms amounts to 1.69 eV.

Table 6. Selected Torsional Angles

compd	torsional angles $|\omega|$ (deg) N(11)−C(112)−C(111)−N(12)	C(15)−C(14)−C(112)−N(11)	C(111)−C(112)−N(11)−C(11)	C(14)−C(15)−C(16)−(17)
ocp (calcd, 6-31G**)	0.3	11.40	7.07	0.0
ocp (exptl, X-ray)	0.59 (0.46)	1.22 (0.32)	2.79 (0.31)	0.18 (0.54)
$Cl_2Hg(ocp)\cdot2.5C_6H_6$	2.60 (0.49)	4.73 (0.35)	6.89 (0.35)	2.60 (0.61)
$[Ag(ocp)_2](PF_6)\cdot CH_2Cl_2$	5.41 (0.55)	4.04 (0.38)	1.55 (0.37)	0.32 (0.68)
$[Cu(ocp)_2](BF_4)$[a]	0.76 (0.87)	1.22 (0.65)	2.55 (0.61)	2.18 (1.15)

[a] From ref 15.

Discussion

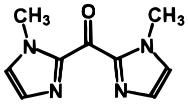
The basic structural arrangements observed in the three d^{10} metal complexes (Cu^I,[12] Ag^I, Hg^{II}) and the crystalline free ligand ocp are not untypical for phenanthrolines and their coordination compounds.[4,8,23] There are the characteristically[4a,e,f,12,24] distorted tetrahedral structures of the $[M(ocp)_2]^+$ cations, the weak binding of the chelate ligand to slightly bent Cl−Hg−Cl (162°), and π/π interaction of individual aromatic molecules in crystals of the free ligand. In agreement with the increasing length of the coordinative bond in the series copper(I) (2.04 Å),[12] silver(I) (2.35 Å), and mercury(II) (2.61 Å), the bite angle N−M−N decreases considerably from 78.8° [12] via 68.2° to 61.2° (Tables 3 and 4). Bond lengths and angles of free or coordinated ocp are also typical for phenanthrene-derived molecules, one typical such feature being the small C(15)−C(16) distance of about 1.36 Å, which indicates a particularly high double-bond character. In free ocp the longest C−C bond is between C(111) and C(112), connecting the pyridine rings (cf. Table 2); this distance is reduced in the complexes through chelate coordination. However, in addition to these more common effects of metal coordination, the ocp ligand exhibits a remarkable qualitative structural variety in its complexes with the d^{10} metal species.

Ocp exhibits significant deviations from planarity of the perchloroheteroaromatic system, both in the free ligand form, where X-ray structural data and *ab initio* results agree rather well (Tables 5 and 6), and as coordinated species in the compounds $[Ag(ocp)_2](PF_6)\cdot CH_2Cl_2$ and $Cl_2Hg(ocp)\cdot2.5C_6H_6$ presented here. Both the dichloromercury(II) complex and the free ligand exhibit saddle-shaped ocp, as illustrated in Figure 4 and Table 6 and as calculated as the absolute energy minimum conformation. The saddle shape is found to be more pronounced in the mercury(II) complex where the perturbation by weakly bound $HgCl_2$ may play a role; on the other hand, the *ab initio* calculation tends to exaggerate the saddle form for the free ligand, which may be due to slightly overestimated Cl- -Cl repulsion forces.[19]

Generally, the most probable reasons for the deviation from planarity are the several nonbonded interactions between neighboring chloride substituents. In the free ligand, for instance, the closest Cl- -Cl contacts are Cl(14)- -Cl(15) (2.937 Å), Cl(13)- -Cl(14) (2.988 Å), and Cl(15)- -Cl(16) (2.980 Å); the other distances between neighboring Cl substituents are slightly longer than 3.00 Å but also smaller than the sum of about 3.6 Å for conventional van der Waals radii.[19,25] The small Cl(14)- -Cl(15) nonbonded distance has its counterpart in the widened bond angle C(13)−C(14)−C(15) of 128.4(3)° (Table 2). For all compounds the torsional angles C(14)−C(15)−C(16)−C(17) are below 3°, which reflects the rather rigid (and short) bond with high double-bond character between C(15) and C(16).

The data in Table 6 reveal that the silver complex ion $[Ag(ocp)_2]^+$ contains an ocp ligand with recognizably twisted pyridyl moieties (Figure 3); the torsional angle N(11)−C(112)−C(111)−N(12) has a relative high value of about 5°. Considering that both the twist and planar structures of free ocp differ by only 2.8 kcal/mol, the difference between the silver complex with twisted ocp ligands and the copper(I) analogue with virtually planar ocp ligands[12] must be due to coordination effects. The essential differences are that Ag^+ is larger than Cu^+ whereas the latter engages in π back-donation to α-diimine chelate ligands.[3,5,26] The larger ionic radius of Ag^+ and the absence of special metal/ligand bonding effects cause ocp to adopt a rather low-energy twist conformation in $[Ag(ocp)_2]^+$, the twist conformation being only 0.4 kcal/mol higher in energy than the saddle arrangement. On the other hand, the smaller Cu^+ ion not only favors a less twisted chelate arrangement but also contains high-lying occupied d orbitals which can back-donate electron density from the metal to the π system of the acceptor ligand.[3,5,26] Optimum π interaction, however, requires a coplanar π system of the acceptor ligand, and the energy gained from this interaction may be sufficient to compensate the small energy amounts necessary for tolerating stronger repulsion. This increased repulsion is obvious from the distinctly smaller Cl- -Cl distances for $[Cu(ocp)_2]^+$ than for free ocp; the lowest value for the copper(I) complex was found at 2.933 Å.[12]

A similar such planarization effect of copper(I) on unsaturated chelate ligands has been described recently for $[Cu(BIK)_2]^+$ ions where BIK is bis(*N*-methylimidazol-2-yl) ketone.[27] Whereas the copper(I) complex ion contains almost coplanar BIK with dihedral angles between the imidazole rings ranging from 2.4° to 8.4°,[27a] the analogous zinc(II) compound exhibits very much twisted BIK ligands with dihedral angles of 25° and 37°.[28]



BIK

According to the electrochemical results reported recently,[12] perchlorination of 1,10-phenanthroline results in a significant stabilization of π^* orbitals, in agreement with the *ab initio* calculation results described above. For complexes such as bis(1,10-phenanthroline)copper(I) both the oxidation and reduction potentials are shifted by about 1 V to more positive values. It

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thus appears that the multiple acceptor effect from eight chlorine substituents lowers the energy of the ligand π^* orbitals and of the metal d orbitals to about the same extent, the latter via diminished σ basicity of the nitrogen lone pairs forming the chelate bonds. Accordingly, the intense metal(d)-to-ligand(π^*) charge transfer (MLCT) absorption of $[Cu(ocp)_2](BF_4)$ occurs at only slightly longer wavelengths than those of organosubstituted analogues.[12] In contrast to many other bis(1,10-phenanthroline)copper(I) complexes[3−5] the perchlorinated complex exhibits no intense luminescence as a solid or in dichloromethane solution.

In agreement with the structural interpretation, the silver complex ion $[Ag(ocp)_2]^+$ is colorless, reflecting both a higher oxidation potential (stabilized HOMO) and a more negative reduction potential (destabilized LUMO) in comparison to the copper analogue.[12]

Summarizing, the flat energy hypersurface around the planar, twisted, and saddle-shaped minimum geometries for ocp implies that small intra- and intermolecular interactions such as metal coordination, molecule/solvent interactions, and crystal packing effects can significantly alter the shape of the ocp ligand. For the free ligand there is good agreement between calculation results and experimental values, both with regard to structure, i.e., the symmetry of the ligand conformation and the detailed bond parameters, and with respect to the electronic situation. Ocp differs from the parent heterocycle by being a better π acceptor but a poorer σ donor. While the steric requirement of the chlorine substituents, especially those in 2,9-positions, conveys an inability to coordinate in octahedral arrangements, (distorted) tetrahedral or trigonal bipyramidal coordination geometries are better suited to apply the special features of that new hydrogen-free acceptor ligand.

Acknowledgment. This work has been supported by Fonds der Chemischen Industrie and Deutsche Forschungsgemeinschaft (DFG), in particular by an exchange program between DFG and the Academy of Sciences of the Czech Republic.

Supporting Information Available: Structure representations (6 pages). One X-ray crystallographic file, in CIF format, is available. Access and ordering information is given on any current masthead page.

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