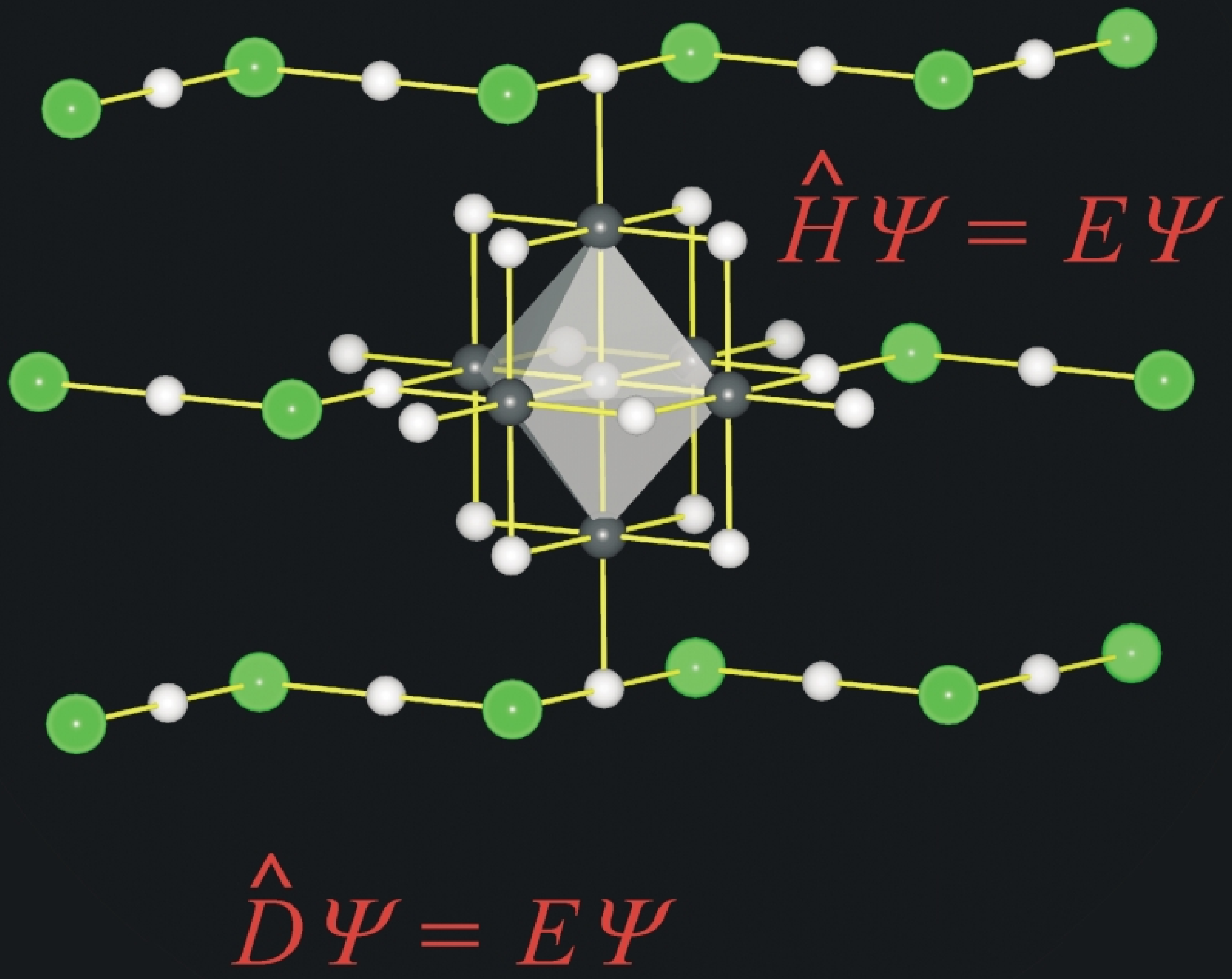
Relativistic effects drastically influence solid-state symmetry: copper and silver halides form cubic or hexagonal structures whereas gold halides form chain structures. Calculations with and without relativistic effects (Dirac and Schrödinger equations, respectively) generate the cubic and chain gold halide structures shown here together.



For more information see the following pages.

Towards the Understanding of Solid-State Structures: From Cubic to Chainlike Arrangements in Group 11 Halides**

Tilo Söhnel, Holger Hermann, and
Peter Schwerdtfeger*

The prediction of crystal structures for atomic and molecular solids is still very difficult[1] and more or less restricted to ionic compounds with weak covalent bonding character.[2] In contrast to molecular structures which can be rationalized in terms of simple bonding models (VSEPR, hybridization, valence electron rules, ionic/covalent/metallic/Van der Waals bonding etc.), such models do not lead to the successful prediction of crystal structures. This can partly be understood from a many-body expansion of the interaction potential between atoms and molecules, where third- or higher-order effects lead to substantial structural differences in the solid state, especially for the metallic state. Moreover, there are often a number of different modifications (polymorphs) separated by only a few kJ mol^{-1}.

The Group 11 halides are particularly interesting. The low-temperature modifications of the copper halides CuCl (nantokite), CuBr, and CuI (marshite) crystallize in a cubic zinc-blende structure with each copper atom coordinated in a tetrahedral arrangement by four halogen atoms.[3] All the silver halides (except AgI) crystallize in a rock-salt structure (Figure 1A) with silver adopting an octahedral coordination sphere.[4] AgI crystallizes in three modifications, the cubic zinc-blende structure (γ-AgI, miersite),[5] the hexagonal wurzite structure (β-AgI, iodargyrite),[6] and a cubic high-temperature modification (α-AgI),[7] which incorporates a molten-silver substructure. In all three cases a tetrahedral coordination sphere around silver is found. The gold halides AuX (X = Cl,[8] Br,[9] I[10]), however, are rather unusual in showing chainlike tetragonal structures (Figure 1B, C) of linear AuX$_2$ units with rather short Au–Au separations attributed to aurophilic interactions.[11]

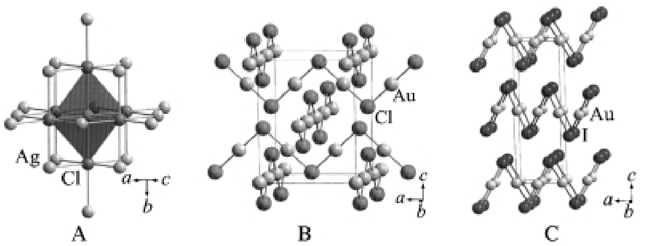


Figure 1. The rock-salt structure of AgCl (A) and the chainlike tetragonal structures of AuCl, chain-I (B), and AuI, chain-P (C).

Relativistic effects are important for Group 11 compounds, especially for gold compounds, and can lead to significant changes in chemical properties.[12] For example, in 1983 Christensen and Kollar pointed out that for CsAu scalar relativistic effects cause a change from a metallic to a semiconducting state with Cs$^+$Au$^-$ becoming ionic and adopting a rock-salt structure.[13] Geipel and Hess showed that for silver halides in the solid state, relativistic effects cannot be neglected, which leads to a decrease of up to 5.8% in molar volumes and to an increase in cohesive energies by up to 8.9%.[14] On the other hand, Doll et al. pointed out that the rock-salt and chainlike AuCl structures are almost energetically degenerate at the Hartree–Fock level of theory, and that electron correlation effects are mainly responsible for the stabilization of the chainlike structure. From coupled-cluster calculations they conclude that this stabilization originates from excitations out of the Au 5d shells which leads to strong correlation effects between Au–Au pairs.[15] In molecules, strong Au–Au (aurophilic) interactions have been attributed to an interplay of dispersion and relativistic effects.[16]

To investigate the origin of these unusual chainlike structures of gold halides we carried out solid-state calculations for all the Group 11 halides MX (M = Cu, Ag, Au; X = F, Cl, Br, I) by using nonrelativistic and relativistic density functional (DFT) and Hartree–Fock (HF) theory (see Experimental Section).

The calculated sublimation energies MX(s) →MX(g) for all known rock-salt, zinc-blende, and wurtzite structures are shown in Figure 2 as a function of the classical dipole–dipole interactions of M$^+$X$^-$ units. These interactions are obtained from the dipole moments of the free molecules and from the M–X bond lengths in the solid state. In Figure 3 the differences in the sublimation energies versus the dipole moments μ of all the calculated MX (M = Cu, Ag, Au; X = F, Cl, Br, I) structures are shown. A number of important points can be deduced from both figures. The sublimation energy of the cubic and the hexagonal structures correlates nicely with the classical static dipole–dipole interaction, which shows that these solid-state compounds are well described as being of ionic nature (Figure 2). In contrast to the cubic and hexagonal structures the sublimation energies of the chainlike structures do not correlate with the classical dipole–dipole interactions. Clearly, these structures contain large covalent bonding contributions which cannot be neglected.

With the exception of the rock-salt AgF structure (which is known experimentally) both CuF and AuF in zinc-blende and AuF in rock-salt modification show unusually low stabilities compared to that expected from the classical dipole interaction model. In the case of AuF, the very low sublimation energy (ΔE_{sub}) of only 147 kJ mol^{-1} for the rock-salt structure (ΔE_{sub} 140 kJ mol^{-1} for the zinc-blende structure or 182 kJ mol^{-1} for the AuCl chainlike structure; see Figures 2 and 3) is the reason why the disproportionation of AuF(s) into AuF$_3$(s) and solid gold is assumed to be exothermic.[17] As previously mentioned the relativistic stabilization of solid gold

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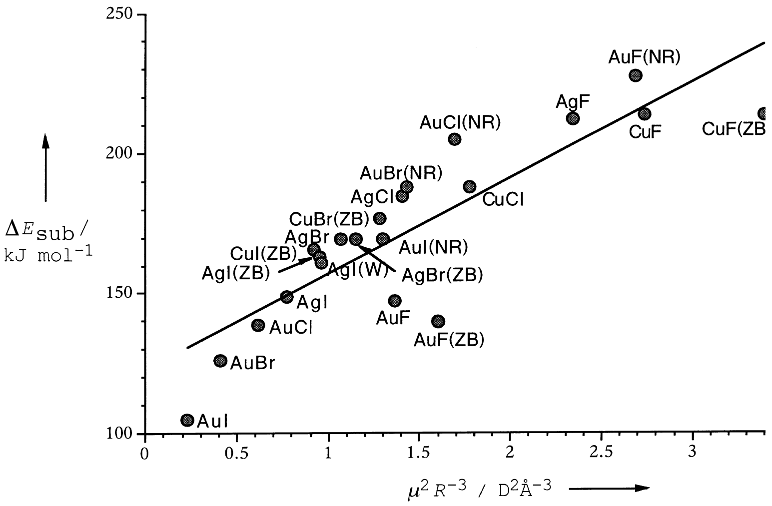

Figure 2. Calculated sublimation energies ΔE_sub (zero Kelvin) versus the classical dipole–dipole interactions (ΔE_sub [kJ mol^{-1}] = $35\mu^2 R(MX)^{-3}$(D^2 Å^{-3}) + 120). If not otherwise indicated the rock-salt structure is taken at the relativistic level of theory. ZB: zinc-blende structure, W: wurtzite structure, NR: nonrelativistic structure. Dipole moments μ taken from molecular AuX data (see Experimental Section), M–X bond distances R are from the optimized solid-state geometries.

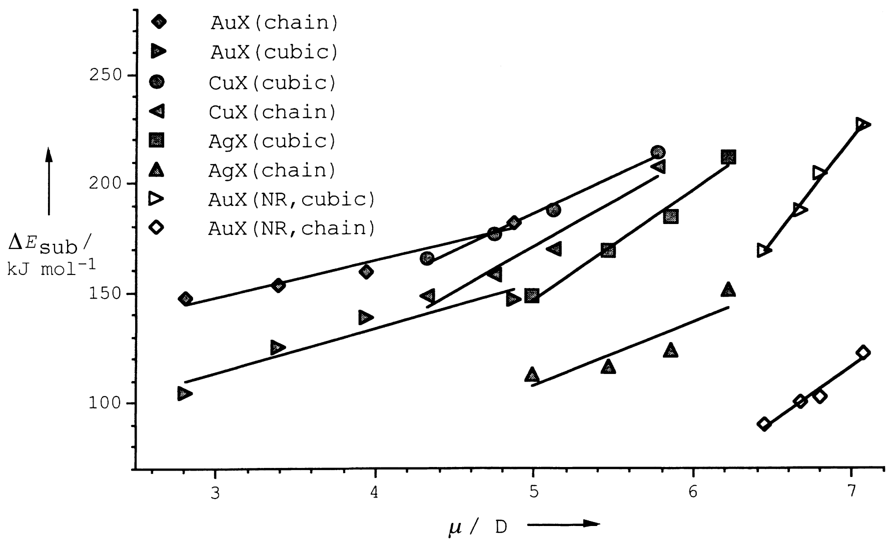

Figure 3. Calculated sublimation energies ΔE_sub (zero Kelvin) versus the molecular dipole moment for the cubic and chainlike structures. See Figures 1 and 2 for details.

is partially responsible for this low sublimation energy.[18] Similar arguments may hold for the disproportionation of CuF(s) into CuF_2(s) and solid copper.

The most important conclusion, however, is that all the gold halides AuX in the cubic (rock salt) structure are relativistically destabilized by up to 80 kJ mol^{-1} (more than 30%) compared to the AuX chain structures (Table 1 and Figure 3). This destabilization is a result of the relativistic increase in the gold electronegativity. The molecular AuX compounds are less ionic (reduction of the dipole moment between 2.2 D for AuF and 3.7 D for AuI) and the static dipole–dipole attraction is diminished significantly. In contrast, for the cubic or hexagonal structures at the nonrelativistic level the sublimation energies increase monotonically from copper to silver to gold (Figure 3).

As mentioned before the chainlike structures are the observed stable modifications for the gold halides AuCl, AuBr, and AuI. It is further clear that the energy difference between the cubic and chain modification is far too large to be explained by Au–Au interactions in the chainlike structure only, as the contribution of the aurophilic attraction in the chain is not expected to amount to more than 25–30 kJ mol^{-1}.[16]

The global minima obtained for the different polymorphic forms all agree with the experimental structures obtained at low temperatures, which demonstrates that for such systems the B3LYP functional is capable of producing accurate results. For example, for AuBr the sublimation energy of the rock-salt structure is 125.7 kJ mol^{-1}, for the chain-I structure (Figure 1) 142.5 kJ mol^{-1}, and for the observed chain-P structure 153.9 kJ mol^{-1}. According to the applied model (see Figure 2) the AgI rock-salt structure, which can only be observed experimentally as one of the high-pressure modifications at a pressure of about 0.4 GPa,[19] appears to be less stable than the experimentally observed zinc-blende and wurzite structure types. Similar to experimental findings the zinc-blende and wurzite modifications (with tetrahedral coordination of the silver atoms) are energetically almost degenerate. In contrast to AgI but in agreement with experiment, AgBr is found to be most stable in the rock-salt structure.

Especially striking are the calculated volumes of the unit cells. In all the copper (CuX) and silver (AgX) structures the higher density is found for the experimentally known cubic structures than for the unknown chain structures. In contrast, for the nonrelativistic gold compounds AuX (X = Cl, Br, I) a higher density is found for the chain structures than for the cubic ones. Higher densities are also found for the relativistic chainlike structures, and these are in good agreement with experimental findings, at least for AuCl ($\rho_\text{exp} = 7.6$ g cm^{-3}) and AuI ($\rho_\text{exp} = 8.25$ g cm^{-3}).[20] For AuBr ($\rho_\text{exp} = 8.2$ g cm^{-3}) the densities of the chainlike structures are slightly smaller than for the cubic one. Jansen and Wiegers conclude from differential thermal analysis (DTA) experiments that there may be another modification of AuBr (α-AuBr) at temperatures $T < 85\,^\circ$C. From their derived lattice constants it is expected that this structurally unknown modification is related to the chain-I structure.[9]

Table 2 shows Mulliken population analyses for the gold compounds in the solid state and the gas phase. There are two important effects in the solid state caused by relativity in gold compounds. All the AuX compounds show a larger Au(6s) population in the scalar relativistic case than in the nonrelativistic case, this is in agreement with molecular results.[11]

Table 1. Calculated bond distances R [Å], dipole moments μ [D], sublimation energies ΔE_{sub} for AuX(s) →AuX(g) [kJ mol^{-1}], and bulk densities ρ [g cm^{-3}].[a]

	AuF		AuCl		AuBr		AuI	
molecule	NR	R	NR	R	NR	R	NR	R
R(AuX)	2.162	2.027	2.538	2.354	2.659	2.512	2.816	2.634
μ	7.1	4.9	6.8	3.9	6.7	3.4	6.5	2.8
solid state Cubic	NR	R	NR	R	NR	R	NR	R
R(AuX)	2.644	2.601	3.010	2.929	3.143	3.038	3.296	3.232
ΔE_{sub}	227.3	146.9	204.6	138.7	187.7	126.1	173.0	104.8
ρ	9.70	10.20	7.08	7.68	7.41	8.20	7.46	7.97
chainlike								
R(AuX)	2.240	2.136	2.517	2.427	2.672	2.563	2.811	2.707
R(AuAu)	2.997	2.994	3.227	3.226	3.067	3.044	3.077	3.076
	3.154	3.151	3.371	3.370				
ΔE_{sub}	122.6	182.1	102.9	159.4	100.4	153.9	90.2	147.9
ρ	9.01	9.03	7.81	7.81	8.05	8.17	8.27	8.28

[a] For AuF and AuCl the chain-I structure and for AuBr and AuI the chain-P structure were taken (see Figure 1). For AuBr we have $\rho = 8.19$ g cm^{-3} for the chain-I structure; NR = nonrelativistic, R = relativistic.

Table 2. Mulliken gross atomic charges q and orbital populations n from B3LYP calculations.[a]

	AuF		AuCl		AuBr		AuI	
molecule	NR	R	NR	R	NR	R	NR	R
q	0.70	0.52	0.55	0.33	0.51	0.28	0.42	0.18
n(5d)	10.0	9.87	10.0	9.95	10.0	9.98	10.0	10.0
n(6s)	0.26	0.56	0.37	0.67	0.41	0.69	0.49	0.80
n(6p)	0.04	0.05	0.05	0.05	0.05	0.05	0.05	0.05
solid state Cubic	NR	R	NR	R	NR	R	NR	R
q	0.74	0.51	0.64	0.42	0.56	0.32	0.47	0.27
n(5d)	9.99	9.99	10.0	10.0	10.0	10.0	10.0	10.0
n(6s)	0.23	0.46	0.31	0.53	0.38	0.63	0.46	0.68
n(6p)	0.03	0.04	0.04	0.05	0.05	0.06	0.06	0.06
chainlike								
q	0.55	0.40	0.29	0.10	0.19	0.02	0.05	−0.10
n(5d)	9.90	9.76	10.0	9.93	10.0	9.93	10.0	9.97
n(6s)	0.46	0.73	0.61	0.86	0.70	0.94	0.80	1.01
n(6p)	0.08	0.10	0.09	0.11	0.10	0.12	0.11	0.12

[a] For AuF and AuCl the chain-I structure and for AuBr and AuI the chain-P structure were taken (see Figure 1); NR = nonrelativistic, R = relativistic.

This result leads to smaller Au atomic charges in the relativistic than in the nonrelativistic calculations. Because of the decreasing electronegativity from F to I the atomic charge of Au decreases in both the relativistic and nonrelativistic case from F to I. The relativistic and nonrelativistic calculations show a larger 6s, a larger 6p, and a smaller 5d population in the chainlike structures than in the cubic structures. This result suggests that the larger 6s/6p populations enhance the Au–Au interactions in the chains. However, the Au–Au distances in the chainlike structures do not decrease significantly from the nonrelativistic to the relativistic cases contrary to what one expects from strong aurophilic interactions. Another important point is that the 5d and 6p participation in the Au–X bond is increased in the chainlike structures compared to the cubic arrangements which indicates an increased covalency in the Au–X bond.

To examine electron correlation effects we carried out HF calculations for AuCl, AuBr, and AuI. Similar to the findings for AuCl, by Doll et al. the cubic and chainlike structures for all the AuX compounds are almost degenerate at the relativistic HF level of theory (in contrast to the nonrelativistic level): (nonrelativistic HF values are given in parentheses) $\Delta E = E_{sub}(\text{cubic}) - E_{sub}(\text{chain}) = 6.4$ (112.7) kJ mol^{-1} for AuCl, −2.9 (97.8) kJ mol^{-1} for AuBr, −11.6 (93.6) kJ mol^{-1} for AuI.

In summary, we conclude that the unusual chainlike structures found for the gold halides AuCl, AuBr, and AuI can alternatively be explained by relativistic effects (as opposed to correlation effects) leading to an increased covalency in the Au–X interactions.

Experimental Section

All solid-state and molecular calculations were carried out with CRYSTAL98.[21] We used scalar relativistic energy consistent small-core Stuttgart pseudopotentials within the density functional theory (DFT, B3LYP-functional) and Hartree–Fock (HF) formalism to estimate electron correlation effects. In addition we carried out nonrelativistic calculations at the DFT and the HF level of theory for the AuX compounds. At the B3LYP level for the Group 11 metals (Cu, Ag, Au) 5s5p5d uncontracted valence basis sets were fitted while for the halogens (Cl, Br, I) 4s4p valence basis sets were developed. For fluorine we optimized a (7s6p) all-electron basis set at the B3LYP level of theory. The geometries of all the structures were optimized with the program code LoptCG developed by Zicovich-Wilson.[22] CuF and AuF are unknown in the solid state and for both compounds the corresponding structure of the chloride was used as a starting point in the geometry optimizations. The dipole moments of the diatomics were taken from ref. [23] when known, otherwise they were calculated at the coupled-cluster (CCSD(T)) level of theory.

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A Metallosupramolecular Capsule with the Topology of the Tetrahedron, 3^3, Assembled from Four Guanidine-Based Ligands and Twelve Cadmium Centers[**]

Iris M. Müller, Richard Robson,[*] and Francis Separovic

Coordination chemistry offers scope for the construction by self-assembly of a seemingly limitless range of structures,[1] including cagelike metallosupramolecular species related to polyhedra.[2] We report here a coordinative enclosure with the topology of the tetrahedron in which the four 3-connecting nodes are provided by extensive, approximately flat ligands, each affording three tridentate metal-binding sites, and the six node-to-node connections are provided by pairs of metal centers; the arrangement is represented schematically in Figure 1.

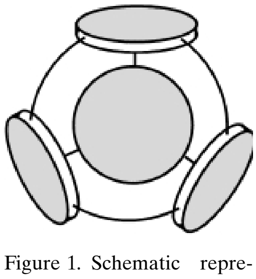
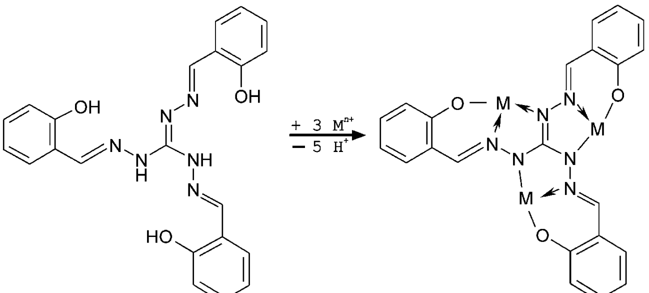


Figure 1. Schematic representation of the cage showing the four almost flat ligands as discs, the central one being at the back. A threefold axis passes throught the center of each disc.

Ligand H_5L (**1**; Scheme 1) is very easy to make and is just one member of a potentially extensive family of Schiff base derivatives of the readily available triaminoguanidine. It has been reported previously that in the presence of appropriate metal cations the central CN_3H_2 core of **1** is readily deprotonated (even by a base as weak as NH_3) to generate a carbonate-like dianionic moiety capable of simultaneously chelating three metal centers in close proximity as in **2** (Scheme 1).[3]



H_5L **1**

$[M_3L]^{3n-5}$ **2**

Scheme 1.

Reaction of the guanidinium chloride salt related to **1**, $[H_6L]Cl$, with cadmium chloride in DMF in the presence of Et_4NOH gives bright yellow rhombic dodecahedral crystals of $(Et_4N)_8[(CdCl)_3L]_4 \cdot 4\,DMF$ (**3**) in very high yield: the structure was determined by single-crystal X-ray diffraction.[4] Figure 2 shows the immediate environment of one of four symmetry-equivalent ligand units. Four $[L(CdCl)_3]^{2-}$ units are linked by four-membered (-Cd-O-)$_2$ rings to form a cage with the topology of a tetrahedron (Figure 3). All twelve cadmium

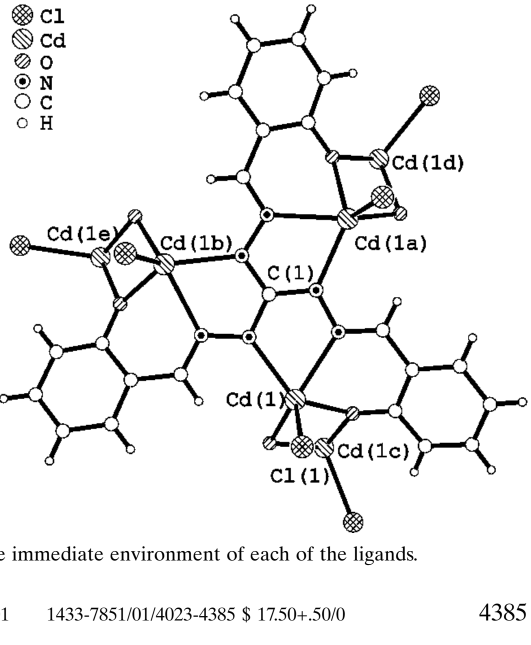


Figure 2. The immediate environment of each of the ligands.

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