

Supplementary Data

A Structure Correlation Study of Four-Coordinate Copper (I) and (II) Complexes.

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Abstract

The geometries of four-coordinate Cu(I) and Cu(II) complexes in the Cambridge Structural Database (CSD) have been analysed systematically and compared using symmetry deformation coordinates and principal component analysis. The observed stereochemistries have been rationalised in terms of the d-electron configurations, interligand repulsion and π -bonding effects. The results confirm that the majority of four-coordinate Cu(I) complexes in the CSD adopt tetrahedral geometries, and deviations from tetrahedral symmetry are caused by the presence of chelating ligands or by the incorporation of copper centres into dimeric or polymetallic structures. Four-coordinate Cu(II) complexes generally adopt geometries that are close to square planar; this is particularly evident for *bis*(chelate) complexes where π -bonding is important. Distortions towards tetrahedral geometries are attributable to steric interactions of bulky substituents in the bidentate ligands.

Supplementary Tables

Table S1. Principal Components for four-coordinate Cu(I) complexes in T_d symmetry.

	PC1	PC2	PC3	PC4	PC5	PC6	PC7	PC8	PC9	PC10
IR	T ₂	T ₂	T ₂	E	E	A	T ₂	T ₂	T ₂	A
% Variance	17.67	17.67	17.67	14.25	14.25	7.78	3.39	3.39	3.39	0.52
R ₁	0.357	0.537	0.516	0.000	0.000	0.440	0.248	0.170	0.182	0.006
R ₂	-0.686	0.336	-0.316	0.000	0.000	0.440	0.151	-0.240	-0.208	0.006
R ₃	-0.195	-0.689	0.412	0.000	0.000	0.440	-0.179	0.229	-0.197	0.006
R ₄	0.524	-0.184	-0.612	0.000	0.000	0.440	-0.219	-0.160	0.223	0.006
θ ₁₂	0.226	-0.599	-0.137	0.180	0.665	-0.019	0.291	-0.050	-0.019	0.093
θ ₁₃	-0.111	0.104	-0.637	-0.666	-0.177	-0.019	0.050	0.291	-0.011	0.093
θ ₁₄	-0.604	-0.243	0.066	0.486	-0.489	-0.019	0.021	0.008	0.295	0.093
θ ₂₃	0.604	0.243	-0.066	0.486	-0.489	-0.019	-0.021	-0.008	-0.295	0.093
θ ₂₄	0.111	-0.104	0.637	-0.666	-0.177	-0.019	-0.050	-0.291	0.011	0.093
θ ₃₄	-0.226	0.599	0.137	0.180	0.665	-0.019	-0.291	0.050	0.019	0.093

Table S2. Principal Components for four-coordinate Cu(LL)L'L" complexes in C_{2v} symmetry.

	PC1	PC2	PC3	PC4	PC5	PC6	PC7	PC8	PC9	PC10
IR	B ₁	A ₁	A ₁	A ₁	A ₂	B ₂	B ₁	A ₁	B ₂	A ₁
% Variance	27.56	23.92	12.29	10.05	7.79	6.71	4.96	4.45	2.01	0.26
R ₁	0.000	0.721	0.021	0.446	0.000	0.452	0.000	0.194	0.198	0.000
R ₂	0.000	0.721	0.021	0.446	0.000	-0.452	0.000	0.194	-0.198	0.000
R ₃	0.413	-0.029	-0.781	0.038	0.000	0.000	-0.466	0.013	0.000	-0.007
R ₄	-0.413	-0.029	-0.781	0.038	0.000	0.000	0.466	0.013	0.000	-0.007
θ ₁₂	0.000	-0.863	0.072	0.110	0.000	0.000	0.000	0.484	0.000	-0.061
θ ₁₃	-0.777	-0.073	0.032	0.223	0.441	-0.256	-0.124	-0.175	0.175	-0.057
θ ₁₄	0.777	-0.073	0.032	0.223	-0.441	-0.256	0.124	-0.175	0.175	-0.057
θ ₂₃	-0.777	-0.073	0.032	0.223	-0.441	0.256	-0.124	-0.175	-0.175	-0.057
θ ₂₄	0.777	-0.073	0.032	0.223	0.441	0.256	0.124	-0.175	-0.175	-0.057
θ ₃₄	0.000	0.765	-0.005	-0.628	0.000	0.000	0.000	0.114	0.000	-0.092

Table S3. Principal Components for four-coordinate Cu(II) complexes in C_{4v} symmetry (8-fold permutation).

	PC1	PC2	PC3	PC4	PC5	PC6	PC7	PC8	PC9	PC10
IR	B ₁	B ₂	A ₁	B ₁	A ₁	E	E	E	E	A ₁
SDCs	S ₂ ,S ₆	S ₃	S ₁ ,S ₅ , S ₀₁	S ₂ ,S ₆	S ₁ ,S ₅ , S ₀₁	S ₄ ,S ₇	S ₁ ,S ₅ , S ₀₁			

% Variance	22.3	15.8	14.2	11.2	10.2	8.6	8.6	4.3	4.3	0.64
R ₁	0.397	0.000	0.498	0.447	0.275	0.349	0.297	0.027	0.330	0.007
R ₂	-0.397	0.000	0.498	-0.447	0.275	0.297	-0.349	-0.330	0.027	0.007
R ₃	0.397	0.000	0.498	0.447	0.275	-0.349	-0.297	-0.027	-0.330	0.007
R ₄	-0.397	0.000	0.498	-0.447	0.275	-0.297	0.349	0.330	-0.027	0.007
θ_{12}	0.000	-0.628	0.320	0.000	-0.422	-0.469	0.038	-0.209	0.245	0.014
θ_{23}	0.000	0.628	0.320	0.000	-0.422	0.038	0.469	-0.245	-0.209	0.014
θ_{34}	0.000	-0.628	0.320	0.000	-0.422	0.469	-0.038	0.209	-0.245	0.014
θ_{14}	0.000	0.628	0.320	0.000	-0.422	-0.038	-0.469	0.245	0.209	0.014
θ_{13}	0.895	0.000	0.089	-0.397	-0.047	0.000	0.000	0.000	0.000	-0.177
θ_{24}	-0.895	0.000	0.089	0.397	-0.047	0.000	0.000	0.000	0.000	-0.177

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