**SUPPLEMENTARY TABLES FOR DEPOSITION**

Table S1 Results from structures in PDB with resolution ≤ 1.2 Å.

a) numbers of contact distances found; all are within ±0.5 Å of the target distance.

| | O *water* | O *asp or glu* | | N *his* | S *cys* | O *carbonyl (main ch)* |
|---|---|---|---|---|---|---|
| Ca | 125 | monodentate | 15 | - | - | 17 |
| | | bidentate | 20 | | | |
| Mg | - | 10 | | - | - | - |
| Fe | 2 | - | | 7 | 32 | - |
| Zn | 4 | 9 | | 9 | 11 | - |

b) Mean value of dif (in Å), where dif is (observed distance - target distance), and sample standard deviation of dif.

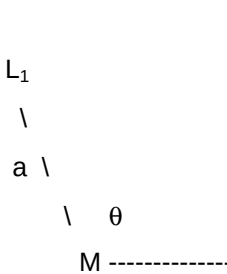
| | | | | | | |
|---|---|---|---|---|---|---|
| Ca | 0.03(5) | monodentate | -0.03(4) | - | - | -0.02(4) |
| | | bidentate | -0.01(5) | | | |
| Mg | - | -0.05(5) | | - | - | - |
| Fe | 0.03(1) | - | | 0.02(5) | 0.01(3) | - |
| Zn | -0.01(2) | -0.02(12) | | 0.02(5) | 0.05(2) | - |

Table S2 Data for restraints or for validation of angles in metalloprotein structures.

a) Number of occurrences, Nobs, of different donor groups in 'representative macromolecules' subset of PDB, structures with resolution $\leq$ 2.8 Å,
Using these, and the target distances from Table 1 the weighted mean M-donor atom distance, M-N,O was derived. Then, using M-S distances from Table 1,
the mean ratio, 1.10 of M-S/M-N,O was derived. [Brackets indicate quantities where very few, if any, observations are available.]

| | O *water* | O *asp or glu* | O *ser or thr* | O *tyr* | O *carbonyl (main chain)* | N *his* | S *cys* | M-N,O (Å) *weighted mean* | M-S(Å) | M-S/M-N,O |
|---|---|---|---|---|---|---|---|---|---|---|
| Ca | 228 | 638 | 38 | - | 316 | - | - | 2.39 | [2.56] | [1.07] |
| Mg | 175 | 153 | 32 | 2 | 19 | 6 | - | 2.18 | [2.23] | [1.02] |
| Mn | 70 | 101 | 1 | - | 2 | 21 | - | 2.23 | 2.35 | [1.05] |
| Fe | 38 | 135 | - | 21 | 7 | 187 | 78 | 2.06 | 2.27 | 1.10 |
| Cu | 3 | 2 | - | 6 | 4 | 94 | 23 | 1.98 | [2.17] | [1.10] |
| Zn | 98 | 179 | 6 | 1 | 16 | 192 | 156 | 2.05 | 2.29 | 1.115 |

b) Calculation of donor-donor distances




$L_1$ and $L_2$ are donor atoms

metal-donor atom distances $M\text{-}L_1 = a$, $M\text{-}L_2 = b$

angle between bonds $L_1\text{-}M\text{-}L_2 = \theta$

donor-donor distance, $L_1 \ldots L_2 = [a^2 + b^2 - 2ab\cos\theta]^{1/2}$

further, if $b = f*a$ where f is a constant $= M\text{-}L_2/M\text{-}L_1$ all L…L distances can be expressed in terms of $M\text{-}L_1$, a and f . ( here f = M-S/M-N,O = 1.10 from above)

if $L_1 = L_2 = N,O$ $L_1 \ldots L_2 = a[2(1 - \cos\theta)]^{1/2}$

if $L_1 = N,O$ and $L_2 = S$ $L_1 \ldots L_2 = a[1 + f^2 - 2f\cos\theta]^{1/2}$

if $L_1 = L_2 = S$ $L_1 \ldots L_2 = af[2(1 - \cos\theta)]^{1/2}$

c) donor-donor distances, $L_1 \ldots L_2$, (in Å) in octahedral, $ML_6$ , coordination (12 angles, $90^o$, and 3 angles, $180^o$)

| | angle, $\theta$, = $90^o$ | | | angle, $\theta$, =$180^o$ | | |
|---|---|---|---|---|---|---|
| | $L_1$ = N,O | $L_1$ = N,O | $L_1$ = S | $L_1$ = N,O | $L_1$ = N,O | $L_1$ = S |
| | $L_2$ = N,O | $L_2$ = S | $L_2$ = S | $L_2$ = N,O | $L_2$ = S | $L_2$ = S |
| $L_1 \ldots L_2$ = | 1.414a | 1.487a | 1.555a | 2.00a | 2.10a | 2.20a |
| Ca | 3.38 | 3.55 | 3.72 | 4.79 | 5.02 | 5.26 |
| Mg | 3.08 | 3.24 | 3.39 | 4.36 | 4.58 | 4.80 |
| Mn | 3.15 | 3.32 | 3.47 | 4.46 | 4.68 | 4.91 |
| Fe | 2.91 | 3.06 | 3.20 | 4.12 | 4.33 | 4.53 |
| $Cu^{II}$ | 2.80 | 2.94 | 3.08 | 3.96 | 4.16 | 4.36 |
| Zn | 2.90 | 3.05 | 3.19 | 4.10 | 4.31 | 4.51 |

Recommendation: restraints should be applied to all distances < 3.8 Å, to 'adjacent' donor atoms in first coordination sphere.
using standard deviations 0.15 Å for Ca, Mg, Mn, Fe and Zn, and 0.30 Å for $Cu^{II}$.

d) donor-donor distances, $L_1 \ldots L_2$, (in Å) in tetrahedral , $ML_4$, coordination ( 6 angles, $109.5^o$)

| | angle, $\theta$, = $90^o$ | | |
|---|---|---|---|
| | $L_1$ = N,O | $L_1$ = N,O | $L_1$ = S |
| | $L_2$ = N,O | $L_2$ = S | $L_2$ = S |
| $L_1 \ldots L_2$ = | 1.633 a | 1.716 a | 1.797 a |
| Mg | 3.56 | 3.74 | 3.92 |
| Mn | 3.64 | 3.83 | 4.01 |
| Fe | 3.36 | 3.53 | 3.70 |
| $Cu^{I}$ | 3.56 | 3.74 | 3.92 |
| Zn | 3.35 | 3.52 | 3.68 |

Recommendation: restraints should be applied to all donor..donor distances, with standard deviation 0.20 Å.
For square planar $Cu^{II}$ distances given above for octahedron may be used.

e) Expected donor-donor distances, $L_1 \ldots L_2$, in 5-coordinate complexes, $ML_5$, with ideal geometry. Distances are given only as the multipliers for a, the M-N,O distance. In the tetp configuration, $105^o$ has been chosen as angle between apical and basal bonds since this is a typical value. It can be seen that even when only one ligand type is present (e.g. N,O but no S) it will not often be practicable to classify and restrain the different L…L distances; only BUMP type restraints are practicable.

| | angles($^o$) | $L_1$ = N,O<br>$L_2$ = N,O<br>$a\,(2 - 2\cos\theta)^{1/2}$ | $L_1$ = N,O<br>$L_2$ = S<br>$a\,(1 + f^2 - 2f\cos\theta)^{1/2}$ | $L_1$ = S<br>$L_2$ = S<br>$a\,f\,(2 - 2\cos\theta)^{1/2}$ |
|---|---|---|---|---|
| tetp | (tetragonal pyramid) | | | |
| | 86 (four) | 1.364 a | 1.431 a | 1.500 a |
| | 105 (four) | 1.587 a | 1.634 a | 1.746 a |
| | 150 (two) | 1.932 a | 2.00 a | 2.125 a |
| tbp | (trigonal bipyramid) | | | |
| | 90 (six) | 1.414 a | 1.449 a | 1.555 a |
| | 120 (three) | 1.732 a | 1.789 a | 1.905 a |
| | 180 (one) | 2.000 a | 2.074 a | 2.200 a |

Table S3 Observations leading to parameters for 'BUMP type restraint in metal coordination complexes. These are based on non-chelated complexes in the CSD, with R ≤ 0.065 Å. Distances were extracted, and their distributions examined, and the mean and standard deviation corresponding to adjacent atoms (i.e. distances < 3.8 Å in octahedral complexes, < 3.6 Å in 5-coordinate complexes) extracted. σ is the sample standard deviation.

| | | *mean (σ)* | *minimum* | *mean of lower part if* | *number* | *proposed* |
|---|---|---|---|---|---|---|
| *$L_1$…$L_2$ (Å)* | *with $L_1$ = $L_2$ =N,O* | | | *distribution composite* | *observations* | *parameters* |
| Ca | in $ML_7$ | 3.10(19) | 2.75 | | 141 | |
| Ca | in $ML_6$ | 3.30(15) | 3.00 | | 162 | |
| Mg | in $ML_6$ | 2.95(6) | 2.84 | | 134 | |
| Mn | in $ML_6$ | 3.11(10) | 2.84 | | 423 | |
| Fe | in $ML_6$ | 3.00(13) | 2.74 | 2.85(6) | 354 | N,O….N,O |
| Cu | in $ML_6$ | 2.99(16) | 2.67 | 2.90(13) or 2.83(6) | 607 | 3.00(15) |
| Zn | in $ML_6$ | 2.98(9) | 2.78 | | 466 | |
| Mn | in $ML_5$ | 3.2(5) | 2.61 | - - - | 19 | |
| Cu | in $ML_5$ | 2.97(20) | 2.61 | 2.85(8) | 275 | |
| Zn | in $ML_5$ | 3.06(21) | 2.82 | 2.97(8) | 42 | |
| | | | | | | |
| *$L_1$…$L_2$ (Å)* | *with $L_1$ = N,O, $L_2$ = S,Cl* | | | | | |
| Mn,Fe,Cu | in $ML_6$ | 3.21(11) | 3.02 | | 71* | |
| Mn,Fe,Cu | in $ML_5$ | 3.10(7) | 2.96 | | 50* | N,O….S,Cl |
| Cu | in $ML_4$(sqp) | 3.12(17) | 2.84 | 3.06(9) | 102** | 3.19(12) |
| Mn,Fe,Cu | in $ML_4$(tet) | 3.45(10) | 3.00 | | 317** | |
| | | | | | | |
| *$L_1$…$L_2$ (Å)* | *with $L_1$ = $L_2$ =S,Cl* | | | | | |
| Mn,Fe,Cu | in $ML_6$ | 3.36(6) | 3.23 | | 45* | |
| Mn,Fe,Cu | in $ML_5$ | 3.29(8) | 3.21 | | 10* | S,Cl….S,Cl |
| Cu | in $ML_4$(sqp) | 3.38(9) | 3.18 | | 315** | 3.38(9) |
| Mn,Fe,Cu | in $ML_4$(tet) | 3.68(12) | 3.40 | | 1353** | |

* all observations are for Cl, none for S. ** most observations are for Cl, only *ca* 10% for S