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SUPPLEMENTARY PUBLICATION

The Geometry of Metal Ligand Interactions Relevant to Proteins:

2 . Angles at the Metal Atom, Additional Weak Metal-donor Interactions

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Abstract

Geometrical data which could be of relevance in the structure determination, structure refinement, assessment or understanding of metalloproteins have been extracted from the Cambridge Structural Database (CSD). The CSD contains crystallographic data from 'small molecule' structures determined by X-ray or neutron diffraction to an accuracy and precision much better than that of most current protein structure determinations. Structures of Mg, Mn, Fe, Cu and Zn complexes with ligands whose donor atoms may be only N,O,S or Cl have been selected, and analysed in terms of the geometry of the metal coordination group - octahedral, tetrahedral, tetragonal pyramid, etc The r.m.s. deviation of all the interbond angles around the metal atom provides a measure, δ, of the deviation from ideal geometry. Average values of δ are tabulated for the different metals, in each type of complex. For simple non-chelated complexes of Mn, Fe and Zn distortions up to 5° in octahedral complexes and 10° in tetrahedral complexes are found to be normal, and seem likely to be a consequence of packing effects, ligand bulk or intramolecular effects. Substantially larger distortions are found for some other metals and geometries, and are common for chelated complexes. Brief comments on 6-, 7- and 8- coordinate Ca complexes are included.

Tables are also presented showing that for 4- and 5-coordinate complexes of Zn and Cu it is quite common to find additional weakly coordinated ligands, usually with N or O donor atoms, and with M...N,O distances longer than a normal bond length, but shorter than a van der Waals contact, e.g. in the range 2.4-3.0 Å for Zn, 2.6-3.0 Å for Cu. Although the contributions to bond valency or bonding energy of such interactions may not be great, their effect on geometry can be considerable; they can, for example, cause much larger distortions of tetrahedral Zn complexes than indicated above.

Fig 3 supplementarty: plots of δ_{tbp} and δ_{tetp} for ML_5 complexes of a)Mn and b)Fe - all conventions as in Fig 3 of main paper.

Table 5 supplementary: refcodes, compound names, references, and distances in $(RCO_2)_2Zn(OH_2)_2$ and $(RCO_2)_2Zn(imidazole)_2$

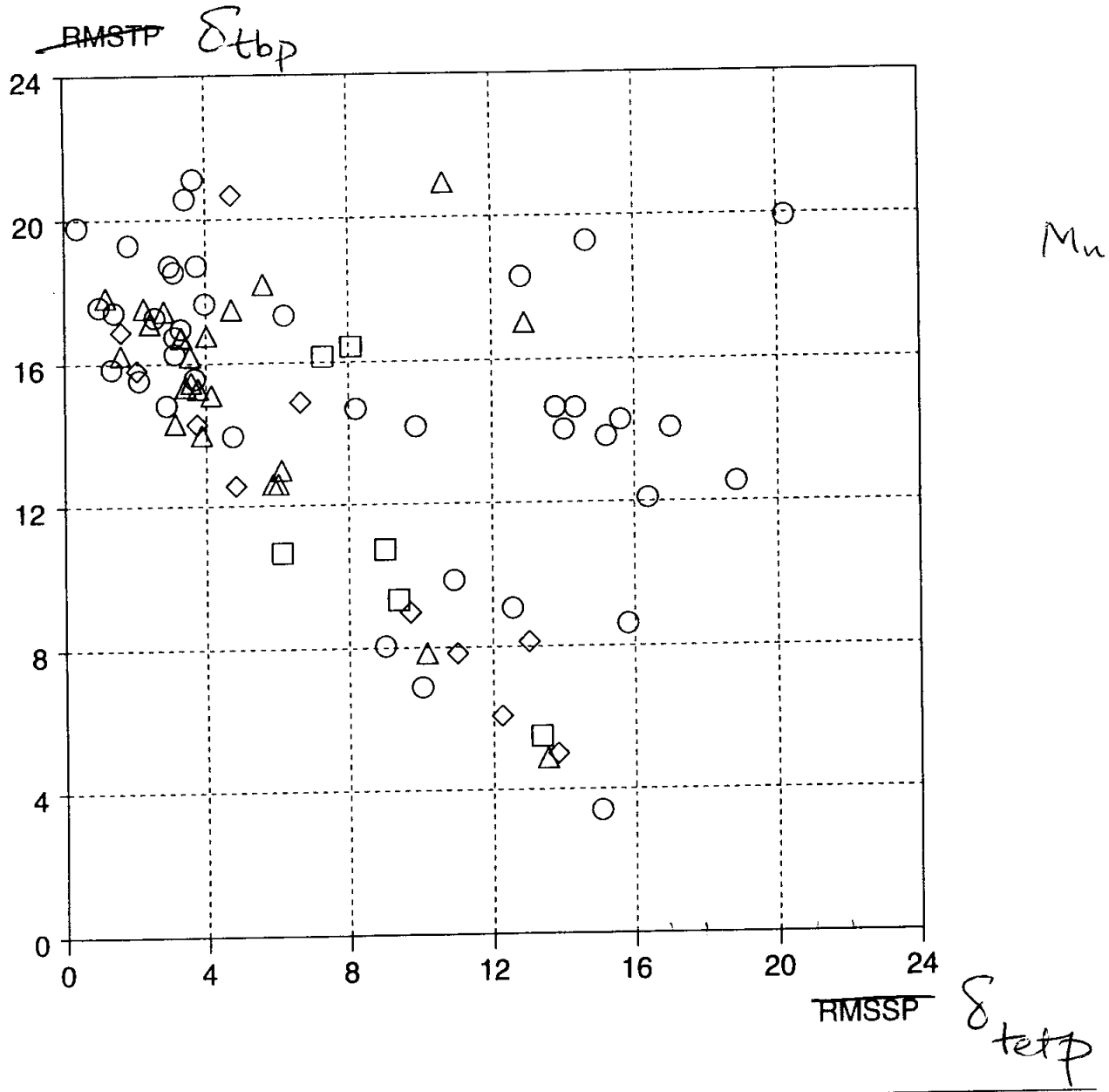

Fig 3 Supplementary

Mn-elevated

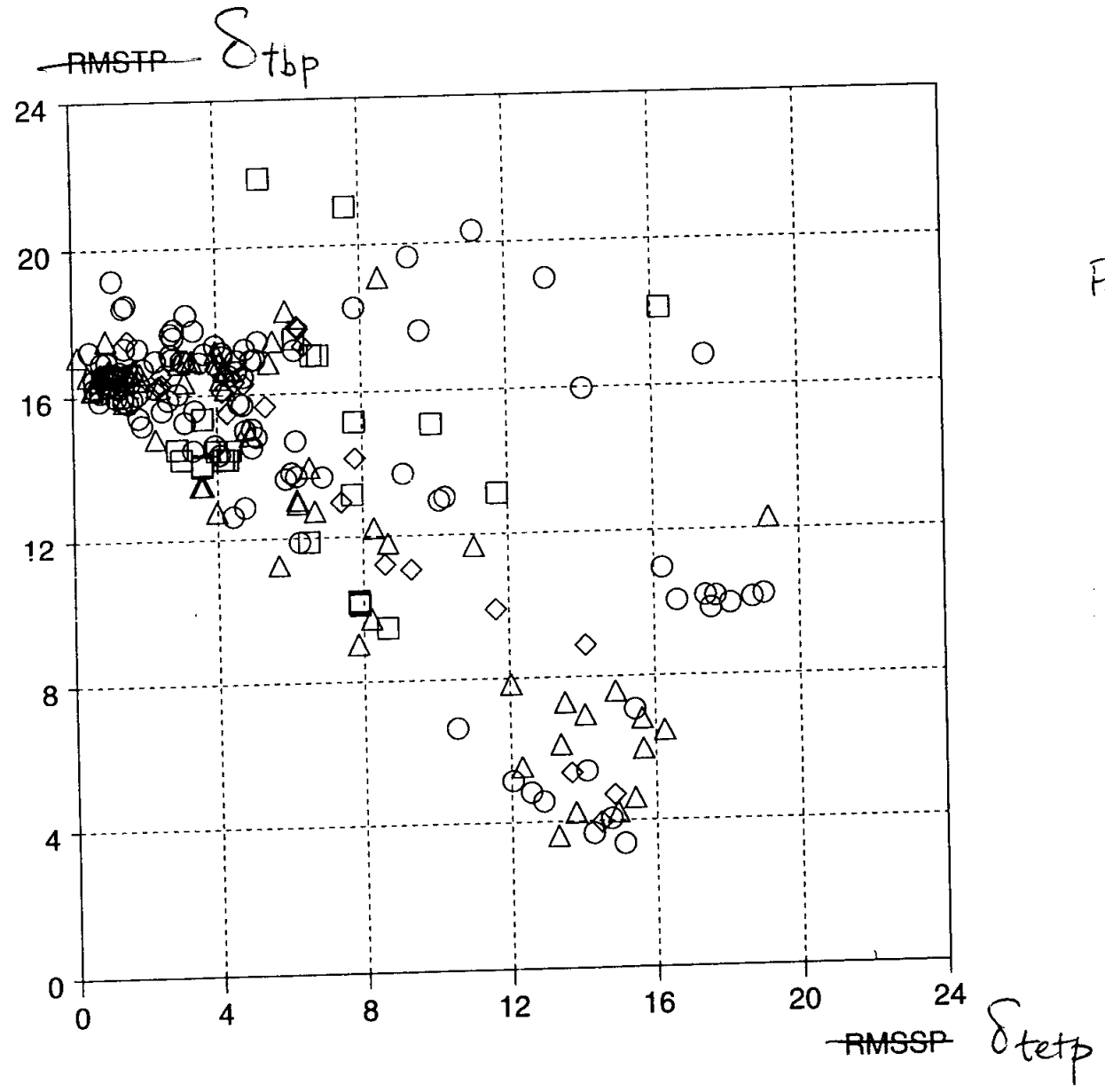

Fig 3 · Supplementary

Fe - chelated

Table 5S - for deposition

Structures of complexes $(RCO_2)_2Zn(OH_2)_2$ and $(RCO_2)_2Zn(imidazole)_2$ used in Fig 5 : refcodes, compound names, references, and Zn..O distances in (A)

FISCUF	2.073	2.381
Diaqua-bis((2-formyl-6-methoxyphenoxy)acetato-O,O')-zinc(ii) C20 H22 O12 Zn1 E.J.O'Reilly,G.Smith,C.H.L.Kennard,T.C.W.Mak Aust.J.Chem., 40, 1147,1987		
HACZIU	1.991	2.456
Diaqua-bis(4-chlorobenzoato)-zinc(ii) C14 H12 Cl2 O6 Zn1 I.Potocnak,M.Dunaj-Jurco,J.Cernak Acta Crystallogr.,Sect.C (Cr.Str.Comm.), 49, 1496,1993		
KALBOO01	1.925	2.866
L-Diaqua-bis(5-oxoprolinato-O)-zinc(ii) absolute configuration, for racemate see PUVDUF C10 H16 N2 O8 Zn1 N.Rodier,R.Ceolin,M.Plat,H.Zumbihl Acta Crystallogr.,Sect.C (Cr.Str.Comm.), 46, 324,1990		
PHXCUB	2.119	2.336
Diaqua-bis(phenoxyacetato)-zinc(ii) C16 H18 O8 Zn1 G.Smith,E.J.O'Reilly,C.H.L.Kennard,K.Stadnicka,B.Oleksyn Inorg.Chim.Acta, 47, 111,1981		
TITWUO	1.944	2.814
Diaqua-bis(N-(p-toluenesulfonyl)-L-glutaminato)-zinc(ii) C24 H34 N4 O12 S2 Zn1 G.Lusvardi,L.Menabue,M.Saladini J.Chem.Cryst., 25, 713,1995		
TORQUM	1.984 1.990	2.515 2.548
Diaqua-bis(acetylsalicylato-O)-zinc C18 H18 O10 Zn1 U.Hartmann,H.Vahrenkamp Bull.Pol.Acad.Sci.,Chem., 42, 155,1994		
ZNASAL01	1.982	2.523
Diaqua-bis(salicylato-O)-zinc(ii) Diaqua-bis(2-hydroxybenzoato-O)-zinc(ii) C14 H14 O8 Zn1 K.Risannen,J.Valkonen,P.Kokkonen,M.Leskela Acta Chem.Scand.Ser.A, 41, 299,1987		
GECZIX	2.138	2.228
Diaqua-bis((benzylthio)acetato-O,O')-zinc(ii) C18 H22 O6 S2 Zn1 Wing-Hong Chan,T.C.W.Mak,Wai-Hing Yip,G.Smith,E.J.O'Reilly,C.H.L.Kennard Polyhedron, 6, 881,1987		
CEHCAT	2.010 2.002	2.522 2.512
Diaqua-bis(p-nitrobenzoato)-zinc(ii) C14 H12 N2 O10 Zn1 G.A.Gusejnov,F.N.Musaev,I.R.Amiraslanov,B.T.Usubaliev,Kh.S.Mamedov Koord.Khim., 9, 1687,1983		
YARKEH	2.107	2.332
Diaqua-bis(4-fluorophenoxyacetato-O,O')-zinc(ii) C16 H16 F2 O8 Zn1 G.Smith,D.E.Lynch,T.C.W.Mak,Wai-Hing Yip,C.H.L.Kennard Polyhedron, 12, 203,1993		
ZNAQAC03	2.179	2.189
Diacetato-diaqua-zinc(ii) at 19.0 deg.K C4 H10 O6 Zn1 T.Ishioka,A.Murata,Y.Kitagawa,K.T.Nakamura Acta Crystallogr.,Sect.C (Cr.Str.Comm.), 53, 1029,1997		
BIVNUP	1.915 1.956	2.821 2.872
Tetra-aqua-bis(2,4-dichlorophenoxyacetato)-zinc(ii) diaqua-bis(2,4-dichlorophenoxyacetato)-zinc(ii) C16 H18 Cl4 O10 Zn1,C16 H14 Cl4 O8 Zn1		

C.H.L.Kennard,G.Smith,E.J.O'Reilly,K.M.Stadnicka,B.J.Oleksyn
Inorg.Chim.Acta, 59, 241,1982

CIWLAV02	2.163	2.229

Diaqua-bis(DL-alpha-lipoato)-zinc(ii)
C16 H30 O6 S4 Zn1
M.R.Baumgartner,H.Schmalle,E.Dubler
Inorg.Chim.Acta, 252, 319,1996

ECBIMB10	1.947	3.151
	1.966	2.692

bis(Propionato)-bis(imidazole)-zinc(ii)
C12 H18 N4 O4 Zn1
W.D.Horrocks Junior,J.N.Ishley,R.R.Whittle
Inorg.Chem., 21, 3265,1982

ECBIMC11	1.966	3.038
	1.991	2.648

bis(Acetato)-bis(imidazole)-zinc(ii)
C10 H14 N4 O4 Zn1
Xiao-Ming Chen,Bao-Hui Ye,Xiao-Chun Huang,Zhi-Tao Xu
J.Chem.Soc.,Dalton Trans., , 3465,1996

GAQYOM	1.969	2.717
	1.949	3.036

bis(1-Methylimidazol-3-yl)-bis(2-pyrrolecarboxylato-O)-zinc(ii)
at 183 deg.K
C18 H20 N6 O4 Zn1
T.A.Zevaco,H.Gorls,E.Dinjus
Polyhedron, 17, 2199,1998

BIYJAU	1.943	2.863
	1.976	2.850

bis(Acetato)-bis(2-ethylimidazolyl)-zinc(ii)
C14 H22 N4 O4 Zn1
W.D.Horrocks Junior,J.N.Ishley,R.R.Whittle
Inorg.Chem., 21, 3270,1982