

treated as additional data in the refinement (see Equation 2.6) and not as parameters. It would appear reasonable to demand the number of restraints to remain significantly lower than the number of independent reflections to make sure that you refine your structure mainly against your diffraction data and not against a large set of restraints, but I cannot see why a crystal structure refinement with more restraints than refined parameters cannot give rise to a sensible and publishable model.

Of course it always depends on what restraints are used and how they are used. As described in Chapter 2 there are two kinds of restraints: direct and relative ones. The former restrain a variable (e.g. an interatomic distance) to a certain target value, while the latter relate variables within the model without imposing any outside values. Relative restraints generally exert much milder influence on the model than direct ones, and even a very large number of justified SADI and DELU restraints cannot jeopardize the ethical integrity of the model. This may be entirely different with direct restraints, and the use of many strong DFIX and ISOR commands to make the model look the way the chemist wants it to, can indeed result in questionable crystal structures.⁵

In general, restraints must be applied with great care and only if justified. When appropriate, however, they should be employed without hesitation, and having more restraints than parameters in a refinement is nothing to be ashamed of.

12.4 Coordination geometries of some cations

Some cations have a characteristic coordination geometry that can help to identify them. Pt^{2+} , for example, is found almost exclusively fourfold coordinated with the four ligands lying in a common plane with the metal atom, while Pt^{4+} prefers octahedral geometry. On the other hand, other cations like lead or molybdenum are rather variable in their geometrical behaviour and it is not all that helpful to memorize all possible geometries. Therefore, the following table is incomplete and contains only a small selection of common cations with their most important coordination geometries. More commonly observed coordination numbers and geometries are printed in boldface, very rarely observed ones have not been included.

Ion	Coordination number	Coordination geometry
Li^+	4	tetrahedral
	6	octahedral
Na^+	4	tetrahedral
	6	octahedral
K^+	4	tetrahedral
	6	octahedral
	>6	various geometries

⁵ George Sheldrick says 'with the right restraints, you can fit an elephant to any data'.

Ion	Coordination number	Coordination geometry
Mg ²⁺	4	tetrahedral
	6	octahedral
Ca ²⁺	6	octahedral
	>6	various geometries
Al ³⁺	4	tetrahedral
	5	trigonal bi-pyramidal
	6	octahedral
Ga ³⁺ /In ³⁺	4	tetrahedral
	5	various geometries
	6	octahedral
Si ⁴⁺	3	planar
	4	tetrahedral
Ti ⁺ /Ti ²⁺	6	octahedral
Ti ³⁺	3	planar
	5	trigonal bi-pyramidal
	6	octahedral
Ti ⁴⁺	4	tetrahedral
Zr ⁴⁺ /Hf ⁴⁺	6	octahedral , trigonal prismatic
	>6	various geometries
V / Nb / Ta in all ox. states	6	octahedral
Cr ³⁺	6	octahedral
Cr ⁴⁺	4	tetrahedral
Mn ⁺ /Mn ⁴⁺	6	octahedral
Mn ⁵⁺ /Mn ⁶⁺ /Mn ⁷⁺	4	tetrahedral
Co ³⁺	6	octahedral
Pd ²⁺ /Pt ²⁺	4	planar
Pd ⁴⁺ /Pt ⁴⁺	6	octahedral
Cu ⁺	4	tetrahedral
Cu ²⁺	4	tetrahedral, planar
	6	octahedral (Jahn-Teller)
Ag ⁺ /Au ⁺ (also Hg ²⁺)	2	linear
Ag ²⁺ /Au ²⁺ /Au ³⁺	4	planar
Zn ²⁺	4	tetrahedral , planar
	6	octahedral
Cd ²⁺	4	tetrahedral
	6	octahedral

12.5 Some typical bond lengths

Below are several tables of some of the more common covalent bond distances, all given in Ångströms.

Single bonds

B	C	N	O	F	Si	P	S	Cl	Br	
1.62	1.58	1.49	1.37	1.32	1.98	1.94	1.81	1.74	1.89	B
	1.54	1.47	1.43	1.39	1.87	1.85	1.83	1.79	1.95	C
		1.45	1.41	1.36	1.74	1.70	1.69	1.75	2.14	N
			1.48	1.42	1.64	1.62	1.57	1.70	1.65	O
				1.42	1.56	1.57	1.54	1.64	1.76	F
					2.34	2.25	2.13	2.02	2.17	Si
						2.22	2.12	2.04	2.22	P
							2.07	2.01	2.24	S
								1.99	2.14	Cl
									2.29	Br

	C(sp³)	C(sp²)	C(sp)	N(sp³)	N(sp²)	O	S	F	Cl	Br
C(sp³)	1.54	1.51	1.46	1.47	1.45	1.43	1.83	1.39	1.79	1.95
C(sp²)		1.47	1.43	1.43	1.40	1.35	1.76	1.35	1.73	1.85
C(sp)			1.37	1.33	1.33	1.26		1.2	1.63	1.79

Double bonds

	C	N	O	P	S
C	1.34	1.29	1.21	1.67	1.63
N		1.25	1.22	1.55	1.52
O			1.21	1.47	1.43
P				2.03	1.92

	C(sp²)	C(sp)	N(sp²)	O	S
C(sp²)	1.34	1.32	1.29	1.21	1.70
C(sp)		1.29	1.20	1.17	1.56

Triple bonds

	C	N	O	P	S
C	1.20	1.16	1.13	1.53	1.47
N		1.10	1.11		

12.6 Resolution tables

From Bragg's law, $\lambda = 2d \sin \Theta$, the relationship between the resolution d and the angle 2Θ can be computed very easily for any given wavelength λ . Below is a table that contains pairs of d [in Å] versus 2Θ [in °] for the two most commonly used anode materials, copper and molybdenum.

Mo Radiation: $\lambda = 0.71073 \text{ \AA}$

2Θ	d	d	2Θ
5	8.15	0.70	61.0
10	4.08	0.75	56.6
15	2.72	0.80	52.7
20	2.05	0.85	49.4
25	1.66	0.90	46.5
30	1.39	0.95	43.3
35	1.18	1.00	41.6
40	1.04	1.10	37.7
45	0.93	1.20	34.8
50	0.84	1.30	32.0
55	0.77	1.40	29.4
60	0.71	1.50	27.4
		2.00	20.5

Cu-Radiation: $\lambda = 1.5418 \text{ \AA}$

2Θ	d	d	2Θ
5	17.67	0.80	149.0
10	8.85	0.85	130.2
20	4.44	0.90	117.9
30	2.98	0.95	108.5
40	2.25	1.00	100.0
50	1.82	1.10	89.0
60	1.54	1.20	79.9