STRUCTURAL SCIENCE
CRYSTAL ENGINEERING
MATERIALS

Volume 75 (2019)

Supporting information for article:

Automated Oxidation-State Assignment for Metal Sites in Coordination Complexes in the Cambridge Structural Database

Matthew G. Reeves, Peter A. Wood and Simon Parsons

S1. Common Oxidation States

Table S1 Thresholds for common oxidation states. True values are those where >15% entries in the CSD have that named value. Bold are common while blue are those observed as defined by C. Housecroft & A. Sharpe (Housecroft & Sharpe, 2001).

15% Threshold		*Valence*							
		i	ii	iii	iv	v	vi	vii	Viii
Metal	*Sc*	FALSE	FALSE	**TRUE**	FALSE	FALSE	FALSE	FALSE	FALSE
	Ti	FALSE	FALSE	FALSE	**TRUE**	FALSE	FALSE	FALSE	FALSE
	V	FALSE	FALSE	TRUE	**TRUE**	**TRUE**	**FALSE**	FALSE	FALSE
	Cr	FALSE	**TRUE**	**TRUE**	FALSE	FALSE	**FALSE**	FALSE	FALSE
	Mn	FALSE	**TRUE**	TRUE	FALSE	FALSE	FALSE	**FALSE**	FALSE
	Fe	FALSE	**TRUE**	**TRUE**	FALSE	FALSE	FALSE	FALSE	FALSE
	Co	FALSE	**TRUE**	**TRUE**	FALSE	FALSE	FALSE	FALSE	FALSE
	Ni	FALSE	**TRUE**	FALSE	FALSE	FALSE	FALSE	FALSE	FALSE
	Cu	**TRUE**	**TRUE**	FALSE	FALSE	FALSE	FALSE	FALSE	FALSE
	Zn	FALSE	**TRUE**	FALSE	FALSE	FALSE	FALSE	FALSE	FALSE
	Y	FALSE	FALSE	**TRUE**	FALSE	FALSE	FALSE	FALSE	FALSE
	Zr	FALSE	FALSE	FALSE	**TRUE**	FALSE	FALSE	FALSE	FALSE
	Nb	FALSE	FALSE	FALSE	TRUE	**TRUE**	FALSE	FALSE	FALSE
	Mo	FALSE	FALSE	FALSE	TRUE	FALSE	**TRUE**	FALSE	FALSE
	Tc	FALSE	FALSE	TRUE	**FALSE**	**TRUE**	FALSE	**FALSE**	FALSE
	Ru	FALSE	TRUE	**FALSE**	FALSE	FALSE	FALSE	FALSE	FALSE
	Rh	TRUE	FALSE	**TRUE**	FALSE	FALSE	FALSE	FALSE	FALSE
	Pd	FALSE	**TRUE**	FALSE	FALSE	FALSE	FALSE	FALSE	FALSE
	Ag	**TRUE**	FALSE	FALSE	FALSE	FALSE	FALSE	FALSE	FALSE
	Cd	FALSE	**TRUE**	FALSE	FALSE	FALSE	FALSE	FALSE	FALSE
	Hf	FALSE	FALSE	FALSE	**TRUE**	FALSE	FALSE	FALSE	FALSE
	Ta	FALSE	FALSE	FALSE	FALSE	**TRUE**	FALSE	FALSE	FALSE
	W	FALSE	TRUE	FALSE	**TRUE**	**FALSE**	**TRUE**	FALSE	FALSE
	Re	TRUE	FALSE	**FALSE**	**FALSE**	**TRUE**	**FALSE**	**FALSE**	FALSE
	Os	FALSE	TRUE	FALSE	**TRUE**	FALSE	TRUE	FALSE	FALSE
	Ir	TRUE	FALSE	**TRUE**	**FALSE**	FALSE	FALSE	FALSE	FALSE
	Pt	FALSE	**TRUE**	FALSE	**FALSE**	FALSE	FALSE	FALSE	FALSE
	Au	TRUE	FALSE	**TRUE**	FALSE	FALSE	FALSE	FALSE	FALSE
	Hg	**FALSE**	**TRUE**	FALSE	FALSE	FALSE	FALSE	FALSE	FALSE

S2. A Worked Bond Valence Sum Method Example

For a full description of how BVS applied to all possible oxidation states, the process is demonstrated here for the four-co-ordinate cobalt complex KUYHES (Akbarzadeh Torbati *et al*., 2010). Application of BVS to each valence is described with a separate table showing how multiple bond valence sums are produced from each of the parameter values available. Each table shows top to bottom combinations which result in seperate bond valence sum values. For each bond encountered, all possible parameters are applied, producing multiple bond valence results. As we iterate through each sucessive bond, a new set of possible pond valences is produced and so a new possible bond valence sum value is also determined. The "best" bond valence sum value, along with the parameter "path" taken to arrive at it are highlighted in green. Note the single set of parameters available for Co(III) in this case, and therefore the single route and BVS value available in Table S3.

Table S2 Possible bond valence combinations for Co(II) assumed valence in CSD Refcode KUYHES.

Co-Cl1 r	2.219															
R0 Parameter	2.033								2.010							
Result	0.605								0.568							
Co-Cl2 r	2.227															
R0 Parameter	2.033				2.010				2.033				2.010			
Result	0.592				0.556				0.592				0.556			
Co-N1 r	2.042															
R0 Parameter	1.720		1.600		1.720		1.600		1.720		1.600		1.720		1.600	
Results	0.419		0.303		0.419		0.303		0.419		0.303		0.419		0.303	
Co-N2 r	2.053															
R0 Parameter	1.720	1.600	1.720	1.600	1.720	1.600	1.720	1.600	1.720	1.600	1.720	1.600	1.720	1.600	1.720	1.600
Results	0.407	0.294	0.407	0.294	0.407	0.294	0.407	0.294	0.407	0.294	0.407	0.294	0.407	0.294	0.407	0.294
Bond Valence Sum	2.022	1.910	1.906	1.794	1.987	1.874	1.871	1.758	1.986	1.873	1.870	1.757	1.950	1.838	1.834	1.721
Delta	0.022	0.090	0.094	0.206	0.013	0.126	0.129	0.242	0.014	0.127	0.130	0.243	0.050	0.162	0.166	0.279

Table S3 Possible bond valence combination for Co(III) assumed valence in CSD Refcode KUYHES.

Co-Cl1 r	2.219
R0 Parameter	2.050
Result	0.633
Co-Cl2 r	2.227
R0 Parameter	2.050
Result	0.620
Co-N1 r	2.042
R0 Parameter	1.690
Results	0.386
Co-N2 r	2.053
R0 Parameter	1.690
Results	0.375
Bond Valence Sum	2.014
Delta	0.986

S3. Confidence Scoring

Table S4 Breakdown of confidence scores for oxidation state assignment in the test dataset.

Confidence	Correct	Incorrect	Total	% Correct
0	0	3113	3113	0.00%
4	8	56	64	12.50%
5	533	2399	2932	18.18%
6	1184	1781	2965	39.93%
7	425	124	549	77.41%
8	891	63	954	93.40%
9	1130	34	1164	97.08%
10	2740	85	2825	96.99%
11	3407	55	3462	98.41%
12	873	18	891	97.98%
13	1106	6	1112	99.46%
14	2363	19	2382	99.20%
15	6203	35	6238	99.44%
16	13038	56	13094	99.57%
17	13171	83	13254	99.37%
Total	47072	7927	54999	85.59%

Summary:

Band	Correct	Incorrect	Total	% Correct
A	35881	199	36080	99.45%
B	8150	192	8342	97.70%
C	2500	1968	4468	55.95%
D	541	2455	2996	18.06%

S4. References

Housecroft, C. E. & Sharpe, A. G. (2001). *Inorganic Chemistry*. Pearson Prentice Hall.

Akbarzadeh Torbati, N., Rezvani, A. R., Safari, N., Saravani, H. & Amani, V. (2010). *Acta Cryst* E**66**, m1284.