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Bond Valence Sum Analysis (BVS) of Metal Ligand Bond Lengths in Some Zn(II), Cd(II) Dithiocarbamate Complexes and Their Adducts

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The chemist wishing to estimate an unknown bond length in a molecule or crystal is confronted with an intimidating array of covalent radii, ionic radii, metallic radii *etc*., from which to choose [1]. The bond valence method [2,3] has recently had considerable success in predicting and interpreting bond lengths in 'ionic solids'. As it can be applied to estimate the bond lengths, *vice-versa* the sum of these bond lengths should give information about the valence of the central ion. In the present study the BVS method is applied to complexes of zinc and cadmium dithiocarbamates to estimate the effective valences of the metal ions from the bond lengths reported from their crystal structures.

The valence v_{ij} of a bond between two atoms i and j is defined so that the sum of all the valences from a given atom i with valence V_i obeys [4] $\Sigma v_{ij} = V_i$. The most commonly adopted relationship for the variation of the bond length d_{ij} with valence is $v_{ij} = \exp[(R_{ij} - d_{ij})/B]$. Here, 'B' is taken to be a universal constant equal to 0.37. The parameter R_{ij} is the bond valence parameter.

The R_{ij} parameters reported by two groups of authors are used in the present calculations. R_{ij} (OK/B) is defined as [5]:

$$R_{ij} = r_i + r_j - \frac{r_i\, r_j[(c_i)^{\frac{1}{2}} - (c_j)^{\frac{1}{2}}]^2}{c_i r_i + c_j r_j}$$

where r_i and r_j are size parameters of the atoms i and j involved in bonding and c_i, c_j are additional parameters associated with atoms i and j such that $R_{ij} = r_i + r_j - f(c_i, c_j, r_i, r_j)$ and if i = j then f = 0. R_{ij}(B/OK) values reported in reference [4] have also been used in the present calculations. The R_{ij} (B/OK) values were deduced from the structural data directly. Similar data reported by Brown and Altermatt [6] did not include the R_{ij} values for Zn–S, Zn–N and Cd–N bonds. Hence, the calculations in the present analysis are limited to the use of the two R_{ij} parameters only viz., R_{ij} (OK/B) and R_{ij} (B/OK),

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(OK/B) and (B/OK) refer to author initials of two papers, who reported R_{ij} values for various M–X bonds [4,5]. Formation of a complex of any metal ion with a multidentate ligand represents a compromise between the steric interactions in the ligand and the steric and electronic requirements of the metal [7]. The bond valence sums (BVS) of the complexes [4] determined from the bond valence parameters [8] account for the valence of the central ion irrespective of the number of bonds and the strength of interactions.

Calculations involving various parameters to determine R_{ij}(OK/B), R_{ij} (B/OK) for the listed complexes and a representative calculation of BVS values are given in Table 1 and 2 respectively. The bond valence sums (BVS) of various complexes are given in Table 3 and 4. BVS values for zinc and cadmium adducts and bisdithiocarbamates are also compared with those whose structures have been reported in the literature.

Table 1. Size parameters.

Bond	R_{ij} (OK/B)	R_{ij} (B/OK)
Zn–S	2.08	2.09
Zn–N	1.77	1.77
Zn–O	1.63	1.70
Zn–I	2.38	2.36
Cd–S	2.28	2.29
Cd–N	1.96	1.96
Cd–I	2.57	2.57

Table 2. BVS values for $[Zn(dedtc)_2]_2$[a].

Bond	d_{ij}	v_{ij} (OK/B)	v_{ij} (B/OK)
Zn–S	2.443	0.374	0.385
Zn–S	2.355	0.475	0.488
Zn–S	2.331	0.507	0.521
Zn–S	2.815	0.137	0.140
Zn–S	2.383	0.440	0.452
	$V_i =$	1.933	1.986

[a] $dedtc^-$ = diethyldithiocarbamate anion.

Valence bond sums of zinc complexes are calculated by making use of two different sets of parameters, reported in the literature. They are Vi(OK/B)(1.90 ± 0.05) and Vi(B/OK)(1.96 ± 0.04) respectively. Examination of the results clearly shows the BVS values to be close to '2', which is equivalent to the formal oxidation state of zinc in the zinc complexes considered. The latter value shows better agreement than the former with respect to the formal oxidation state of the central ion. The bond valence sum values are greater in the parent zinc dithiocarbamate complexes than the adducts. But, considering the esd's associated with the bond distances, the value can be assumed to be close to 2.0 without any serious error [28]. Therefore, both values are close to 2.0 indicating the valence of the zinc ion in the complex, irrespective of the coordination number. VBS values for the four coordinate $Zn(bipiptds)I_2$ are the largest: 2.00(OK/B) and 1.96(B/OK). The five coordinate parent dithiocarbamates and six coordinate adducts show low BVS values relatively. Particularly, the six coordinate, 2,2′-bipyridine and 1,10-phenanthroline adducts show BVS values close to 1.84 ± 0.05. Apparently, there is an increasing trend in BVS values for zinc in these compounds as the coordination decrease from 6 to 4. But in all the cases the valency of the central zinc ion is close to 2. Change in coordination number and change in coordination environment around the zinc ion in the complexes have adjusted themselves in such a way that the valency of the central ion is satisfied. Similarly, the two BVS values Vi(B/OK)(2.01 ± 0.05), Vi(OK/B)(1.96 ± 0.04) are close to 2.0 for the cadmium complexes. The BVS value has been found to be close to 2.0 in all the cadmium complexes, irrespective of the coordination number, which confirms the valency of the cadmium in the complexes to be 2.0. The BVS analysis for the bisdithiocarbamates of zinc and cadmium and their adducts shows the valency of the central metal to be 2.0 as expected. This confirms the correctness of the related crystal structures. However, in the process, the valence of the central ion is fulfilled and the situation justifies the statement " formation of a complex involving metal ion and multidentate ligands represents a compromise between the steric interactions in the ligand and the steric and electronic requirement of the metal ion".

Table 3. Bond Valence Sums for zinc complexes[d].

Compound	Coordination number	V_i (OK/B)	V_i (B/OK)	Ref. [b]
$[Zn(dedtc)_2]_2$	4[a]	1.94	1.99	9
$[Zn(dmdtc)_2]_2$	4[a]	1.96	2.01	10
$[Zn(deadtc)_2]_2$	4[a]	1.88	1.93	11[c]
$[Zn(dipdtc)_2]_2$	4[a]	1.94	1.97	12
$[Zn(dnpdtc)_2]_2$	4[a]	2.02	2.08	13
$[Zn(dmdtc)(C_7H_4NS_2)_2]^-$	4[a]	1.91	1.94	14
$[Zn(bipiptds)I_2]$	4	2.00	1.96	15[c]
$[Zn(dmdtc)_2(py)]$	5	1.94	1.98	16
$[Zn(dmdtc)(\mu\text{-}OCOMe)]^-$	5	1.83	1.95	17
$[Zn(dmdtc)_2(2,2'\text{-}bipy)]$	6	1.84	1.87	29
$[Zn(dmdtc)_2(1,10\text{-}phen)]$	6	1.86	1.89	29
$[Zn(pipdtc)_2(2,2'\text{-}bipy)]$	6	1.85	1.89	18[c]
$[Zn(mdtc)_2(2,2'\text{-}bipy)]$	6	1.84	1.88	19[c]
$[Zn(S_2CNMe^iPr)_2(py)]$	5	1.95	1.99	20
$[Zn_2(S_2CNMe^iPr)_4(TMED)]$	5	1.84	1.89	20
$[Zn_2(nmedtc)_4(4,4'\text{-}bipy)]$	5	1.94	1.99	30
$[Zn_2(deadtc)_4(4,4'\text{-}bipy)]$	5	1.92	1.96	30

[a] Actual coordination number is five including a long Zn–S bond.

[b] The crystal structure data of the complexes were obtained from the corresponding literature.

[c] Work reported from our laboratory.

[d] See Table 4.

Table 4. Bond Valence Sums for cadmium complexes[d].

Compound	Coordination number	V_i (OK/B)	V_i (B/OK)	Ref. [b]
$[Cd(dedtc)_2]_2$	4[a]	2.03	2.09	21
$[Cd(S_2CNC_6H_{12})_2]_2$	4[a]	1.98	2.04	22
$[Cd(deadtc)_2]_2$	4[a]	1.97	2.02	23[c]
$[Cd(bipiptds)I_2]$	4	2.14	2.16	15[c]
$[Cd(S_2COEt)_2(1{,}10\text{-phen})]$	6	1.97	2.00	24
$[Cd(S_2CSBu)_2(2{,}2'\text{-bipy})]$	6	2.02	2.05	25
$[Cd(pipdtc)_2(1{,}10\text{-phen})]$	6	2.00	2.03	26[c]
$[Cd(pipdtc)_2(2{,}2'\text{-bipy})]$	6	2.03	2.07	26[c]
$[Cd(mdtc)_2(1{,}10\text{-phen})]$	6	2.00	2.03	27[c]
$[Cd(pipdtc)_2]_2$	4[a]	2.02	2.07	31
$[Cd(deadtc)_2(2{,}2'\text{-bipy})]$	6	2.05	2.09	23

[a] Actual coordination number is five including a long Cd–S bond.

[b] The crystal structure data of the complexes were obtained from the corresponding literature.

[c] Work reported from our laboratory.

[d] $dedtc^-$ = $Et_2NCS_2^-$, $dmdtc^-$ = $Me_2NCS_2^-$ $deadtc^-$ = $(HOCH_2CH_2)_2$ NCS_2^-, $dipdtc^-$ = $[(CH_3)_2CH]_2$ NCS_2^-, $dnpdtc^-$ = $(H_3CCH_2CH_2)_2$ NCS_2^-, $pipdtc^-$ = $H_{10}C_5NCS_2^-$, $mdtc^-$ = $OH_8C_4NCS_2^-$, $nmedtc^-$ = $HOCH_2CH_2(CH_3)$ NCS_2^-, TMED = Tetramethylethylenediamine, bipiptds = piperidinethiuramdisulphide.

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