Bond-Valence Approach to the Metal-Sulphur and Metal-Nitrogen Bonding Systems in Zinc and Cadmium Dithiocarbamate Complexes

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Abstract : The bond valence sum method (BVS) is popular method in coordination chemistry to estimate the oxidation states of atoms. A simple method for determining the oxidation state of the Zn and Cd in complexes involving only N, S donors using the bond valence sum, henceforth BVS, is proposed. The bond distances for a series of Zinc(II) and Cadmium(II) dithiocarbamate complexes and their nitrogenous adducts have been collected from the literature and analyzed using the bond valence sum method to calculate the oxidation state of the metal ion in the complexes. The BVS analysis has confirmed the valency of the central metal to be 2.0 as expected and proves the correctness of the related crystal structures.
Keywords : Crystallographic distances, Bond Valence Sums, Dithiocarbamate, Zinc, Steric effect.

Introduction

If BVS method is used with chemical sense, it will give   valuable additional information about the crystal structures, because of the interplay of bonding and structural exigencies that influences the interatomic distances in a crystal structure. By using the well known interatomic bond lengths from a crystal structure the necessary calculations can be performed with a pocket ruler. BVS method is traditionally used to calculate the oxidation state of a central atom, if the bond valence parameter (R_{ij}) value and the bond length values from donor atoms to the central atom are known. This method is extremely useful to all chemists in resolving conflicts regarding oxidation states or in evaluating the results of a crystal structure analysis [1-10].

In a signifcant number of cases the information based on BVS analysis is sufficient to make accurate predictions about the real crystal structure of the compound. 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 [11]. The bond valence method [12,13] 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. Using the crystallographic data reported by our research group, the BVS calculations were made and results were published for a series of zinc and cadmium dithiocarbamate complexes and their adducts [14-25]. The BVS investigations for divalent zinc and cadmium dithiocarbamte complexes resulted in excellent agreement with the formal oxidation state of the metal. The observation is a clear case of a more or less ionic interaction prevailing in metallo-organic compounds involving d^{10} metal ions. In continuation of our interest to estimate the effective valence of the metal ion and confirming the correctness of the crystal structures of the metal dithiocarbamate complexes, the crystallographic distances for a series of zinc, cadmium dithiocarbamate complexes and their nitrogenous adducts have been collected from the literature and analyzed.

The BVS method

For inorganic compounds, the bond valence v_{ij} is a more accurate description than the strict bond order. 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 Vi obeys [26] $\sum v_{ij} = V_i$. 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.. For inorganic compounds, including those of transition metals, the parameter B is commonly accepted to have a value of 0.37 A°. 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 [27]:

$$R_{ij} = r_i+r_j-[r_ir_j(\sqrt{c_i}-\sqrt{c_j})^2]/[c_ir_i+c_jr_j]$$

Where r_i and r_j are size parameters of the atom 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. The $R_{ij}(B/OK)$ values were deduced from the structural data directly. Similar data reported by Brown and Altermatt [28] did not include the R_{ij} values for Zn-S, Zn-N and Cd-N bonds. The calculations in the present analysis are limited to the use of the two R_{ij} parameters only viz., $R_{ij}(OK/B)$ and $R_{ij}(B/OK)$, (OK/B) and (B/OK) refer to author initials of two papers who reported R_{ij} values for various M-X bonds [26,27]. Coordination complex formation between any metal ion and a multidentate ligand represents a compromise between the steric and electronic requirements of the metal ion and steric interactions in the ligand [29]. BVS of the complexes [26] determined from the bond valence parameters [30] account for the valence of the central ion irrespective of the number of bonds and the strength of interactions.

Results and Discussion

Valence bond parameters (R_{ij}) values for Zn-S, Zn-N, Cd-S and Cd-N bonds and a representative calculation of BVS values are given in Table 1 and 2 respectively. The bond valence sums (BVS) of zinc and cadmium complexes are given in Table 3 and 4. Bond Valence Sums are calculated for the zinc complexes by making use of two different sets of parameters such as $V_i(OK/B)$ and $V_i(B/OK)$ reported in the literature. Investigation of the results reveals the BVS values to be close to'2' which is equivalent to the formal oxidation state of zinc in the complexes considered. The latter value ($V_i(B/OK)$) shows better agreement than the former with respect to the formal oxidation state of the metal ion. BVS values $V_i(OK/B)$ and $V_i(B/OK)$ are close to 2.0 indicating the valence of the zinc in the complexes, irrespective of the coordination number. Change in coordination number and change in coordination environment around the metal ion in the complexes have adjusted themselves in such a way that the valency of the central ion is satisfied.

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
Cd-S	2.28	2.29
Cd-N	1.96	1.96

OK/B = calculated by the method due to O'Keeffee and Brese
B/OK = calculated by the method due to Brese and O'Keeffee

Table 2. BVS values for Zn[S₂CN(n-Pr)(ᶦBu)]₂ (1,10-Phen)

Bond	d_{ij}	$v_{ij}(OK/B)$	$v_{ij}(B/OK)$
Zn-S	2.491	0.329	0.338
Zn-S	2.493	0.328	0.336
Zn-S	2.507	0.315	0.324
Zn-S	2.531	0.295	0.304
Zn-N	2.199	0.313	0.313
Zn-N	2.213	0.302	0.302
	$V_i =$	1.882	1.917

Table 3. Bond Valence Sums for Zinc Complexes

Compound	Coordi nation number	V_i(OK/B)	V_i(B/OK)
Zn[S_2CN(n-Pr)(^iBu)]$_2$	4 [a]	1.98	2.03
Zn[S_2CNPh_2]$_2$	4 [a]	2.35	2.42
Zn[$S_2CN(CH_2)_4$]$_2$	4 [a]	1.90	1.95
Zn[$S_2CN(Me)(CH_2CH_2OH)$]$_2$	4 [a]	1.93	1.98
Zn[S_2CN(n-Pr)(^iBu)]$_2$ (1,10-Phen)	6	1.88	1.92
Zn$_2$[($S_2CN(^iPr)_2)_4$]($C_{12}H_{10}N_2$)	5	1.94	1.98
Zn$_2$[($S_2CNMe_2)_4$]($C_{12}H_{10}N_2$)	5	1.96	2.00
Zn$_2$[($S_2CN(^iPr)_2)_4$]($C_{12}H_{12}N_2$)	5	1.90	1.94
Zn$_2$[($S_2CN(Me)(Et)_4$]($C_{10}H_8N_2$)	6	1.87	1.90
Zn[S_2CNMe_2]$_2$($C_5H_{11}N$)	5	1.82	1.85
Zn[$S_2CN(Et)_2$]$_2$($C_5H_{11}N$)	5	1..93	1.97
Zn[$S_2CN(Et)_2$]$_2$[NH(i-$C_4H_9)_2$]	5	1.93	1.97
Zn[$S_2CN(Et)_2$]$_2$(C_4H_9NO)	5	1.94	1.98
Zn[(4-mpipdtc)$_2$(TMED)]	6	1.70	1.73
Zn[$S_2CN(Me)(Ph)$]$_2$($C_{10}H_8N_2$)	6	1.96	1.98
Zn[S_2CN(n-Pr)$_2$]$_2$ ($C_{12}H_8N_2$)	6	1.95	1.98
Zn[S_2CN(n-Pr)$_2$]$_2$($C_{10}H_8N_2$)	6	1.94	1.97
Zn[$S_2CN(Me)(CH_2CH_2OH)$]($C_{18}H_{12}N_6$)	5	1.97	2.00

* The Crystal structure data of the complexes were obtained from the corresponding literature. [a] Actual coordination number is five including a long Zn-S bond.

Table 4. Bond Valence sums for Cadmium Complexes.

Compound	Coordi nation number	V_i(OK/B)	V_i(B/OK)
Cd[$S_2CN(CH_2)_5$]$_2$	4 [a]	2.05	2.10
Cd[$C_{13}H_{12}NOS_2$]$_2$	4 [a]	2.00	2.06
Cd[S_2CN(n-Pr)($CH_2CH_2OH)_2$($C_{10}H_8N_2$)	6	2.04	2.08
[Cd($C_{14}H_{20}NS_2)_2$($C_{10}H_8N_2$)]	6	2.03	2.06
[Cd($C_{14}H_{20}NS_2)_2$($C_{12}H_8N_2$)]	6	2.00	2.05
[Cd($C_6H_{11}N_2S_2)_2$($C_5H_5N)_2$]	6	1.97	2.01
[Cd(thqdtc)$_2$($C_{10}H_8N_2$)]	6	2.05	2.09
[Cd(thqdtc)$_2$($C_{12}H_8N_2$)]	6	2.06	2.10
Cd[$S_2CN(Me)(^iPr)_2$]($C_{10}H_8N_2$)	6	2.00	2.04
[Cd(mpipdtc)$_2$($C_{10}H_8N_2$)]	6	1.98	2.02
[Cd(epipdtc)$_2$($C_{10}H_8N_2$)]	6	1.97	2.02
Cd[S_2CN(n-Bu)$_2$] ($C_{10}H_8N_2$)	6	2.04	2.08
Cd[$S_2CN(^iBu)$(n-Pr)]$_2$($C_{10}H_8N_2$)	6	1.97	2.01

*The Crystal structure data of the complexes were obtained from the corresponding literature.
[a]Actual coordination number is five including a long Cd-S bond.
^-S_2CN(n-Pr)^iBu=N-sec-butyl-N-n-propyldithiocarbamate anion, $^-S_2CNPh_2$ = N-phenyl-N-phenyldithiocarbamate anion, $^-S_2CN(CH_2)_4$ = pyrrolidinedithiocarbamate anion, $^-S_2CN(Me)CH_2CH_2OH$ = N-Methyl-,N-ethanoldithiocarbamate anion, $^-S_2CN(^iPr)_2$ = *N*,*N*-diisopropyldithiocarbamate anion, $^-$ $^-S_2CNMe_2$ = *N*,*N*-dimethyldithiocarbamate anion, $^-S_2CN(Me)Et$ = *N*-ethyl-*N*-methyldithiocarbamate anion, $^-S_2CN(Et)_2$ = *N*,*N* –diethyldithiocarbamate anion, $^-S_2CN(Me)Ph$ = N-methyl-N-phenyldithiocarbamate anion, ^-S_2CN(n-Pr)$_2$=di-n-propyldithiocarbamate anion, $^-S_2CN(CH_2)_5$ =N,N-pentamethylenedithiocarbamate anion, $C_6H_{11}N_2S_2^-$ = 4-methylpiperazinedithiocarbamate anion,$^-$ $C_{13}H_{12}NOS_2^-$ = *N*-benzyl-*N*-furfuryldithiocarbamate anon, ^-S_2CN(n-Pr)CH_2CH_2OH = *N*-(2-hydroxyethyl)-*N*-propyldithiocarbamate anion, $C_{14}H_{20}NS_2^-$ = Diallyldithiocarbamate anion, thqdtc$^-$ = 1,2,3,4-tetrahydroquinolinedithiocarbamate anion, $^-S_2CN(Me)^iPr$ = *N*-isopropyl-*N*-methyldithiocarbamate anion, mpipdtc$^-$ = methylpiperidinedithiocarbamate anion, epipdtc$^-$ =

ethylpiperidinedithiocarbamate anion, $S_2CN(nBu)_2$=N,N-di-n-butyldithiocarbamate anion, $C_{12}H_8N_2$ = 1,10-Phenanthroline, $C_{12}H_{10}N_2$ = Di-4-pyridylethylene, $C_{12}H_{12}N_2$ = Di-4-pyridylethane, $C_{10}H_8N_2$ = 2,2'-Bipyridine, 4,4'-bipy = 4,4'-Bipyridine, $C_5H_{11}N$ = Piperidine, $NH(i\text{-}C_4H_9)_2$ = Diisobutylamine, C_4H_9NO = Morpholine, TMED = Tetramethylethylenediamine, $C_{18}H_{12}N_6$ = 2,4,6-tris(pyridin-2-yl)-1,3,5-triazine, $C_{12}H_{10}N_4$ = Pyridinealdazine, C_5H_5N = pyridine

Generally the BVS values for adducts are lower than the parent zinc dithiocarbamates [15, 18, 25]. It is owing to the longer distances of Zn-S in the case of adducts than the $Zn(dtc)_2$ complexes due to the presence of an additional neutral ligands. This trend weakens the Zn-S distances in the adducts and this is very well in keeping with the decreased BVS values. But, interestingly the BVS values for Tetramethylethylenediamine adduct, [Zn(m-Pipdtc))$_2$(TMED)], are significantly lower [(V_i(OK/B =1.70) and V_i(B/OK = 1.73)] than the values obtained for other adducts. This interesting trend is due to the bulkiness of the   dimethylamino units of TMED may inhibit the approach of the ligand to the zinc atom due to steric effect and result in a very longer Zn-N bond lengths, which reflect on decreased BVS values.   It has also been observed that the central zinc atom in the dimeric structure, $[Zn_2(C_{11}H_{14}NS_2)_4]$ ($C_{11}H_{14}NS_2^-$ = N-phenyl-N-phenyldithiocarbamate anion), shows BVS values of 2.35 (OK/B); 2.42 (B/OK), which are significantly higher than the values obtained for other parent zinc dithiocarbamate complexes. The increase in BVS values can be ascribed to the decrease in Zn–S distances due to the steric nature of more phenyl groups present in the ligand.

Unusually, in the case of [Zn(S$_2$CN(Me)CH$_2$CH$_2$OH)$_2$(C$_{18}$H$_{12}$N$_6$)] ($C_{18}H_{12}N_6$ = 2,4,6-tris(pyridin-2-yl)-1,3,5-triazine), the BVS values are higher than the values obtained for the parent complex. The increase may be due to the effective tridentate coordination of 2,4,6-tris(pyridin-2-yl)-1,3,5-triazine ligand through its three nitrogen atoms and coordination from sulphur atoms of dithiocarbamate ligands.

In all the cadmium complexes, the BVS values have been found to be close to '2' irrespective of the coordination numbers, which confirm the valency of the cadmium in the complexes. Also it has been found that in the cadmium dithiocarbamate complexes and their adducts no observable changes are seen in BVS values. Due to larger size of cadmium ion compared to zinc ion, the Cd-S distances are not much affected by the change in coordination geometry. 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 crystal structures reported in the literature. 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 requirements of the metal ion.

Conclusions

Bond valence sum (BVS) is used by many researchers to determine the oxidation state of metal ions in solids based on crystallographically determined metal-ligand bond distances. For a series of Zinc(II) and Cadmium(II) dithiocarbamate complexes and their nitrogenous adducts, the crystallographic bond distances have been collected from the literature and analyzed using the BVS method to calculate the oxidation state of the metal ion in the complexes. As expected, the BVS investigation has confirmed the valency of the central metal to be 2.0..

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