



Assignment of Oxidation States of Metal Ions in Zinc and Cadmium Dithiocarbamate Complexes and their Adducts

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ABSTRACT

In this paper we have taken the initiative to assign the oxidation state of metal ions in Zinc and Cadmium dithiocarbamate complexes by using Bond Valence Sum (BVS) method. For that the crystallographic distances for a series of Zn(II) and Cd(II) dithiocarbamate complexes and their nitrogenous adducts have been collected from the literature and analyzed using the bond valence sum method. The calculated values from crystallographic distances predict the correct oxidation state of the metal centre in a wide range of structural types. 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: Oxidation state, Bond Valence Sums, dithiocarbamate, Zinc, Cadmium

INTRODUCTION

The bond valence sum method is popular method in coordination chemistry to estimate the oxidation states of atoms. This method relates the bond lengths around a metal center to its oxidation state. Historically from the concept of bond number, this method was originally propounded by Pauling¹. Later I. D. Brown and other scientists further fleshed it out²⁻⁶. The advantage of this approach is that the bond length is a unique function of bond valence. Generally for a particular bond type, the bond valence diminishes exponentially as the bond length increases. In this semi-empirical method, the valence 'v' of a bond

between two given atoms i and j is related by an empirical relation

$$v_{ij} = \exp[(R_{ij}-d_{ij}/B)] \quad \dots(1)$$

where d_{ij} is the bond distance in Å and R_{ij} is a parameter characteristic of the bond. Like d_{ij} , R_{ij} is known as the bond valence parameter with the same unit in Å. R_{ij} parameter is coordination number and geometry specific. Here 'B' is considered as universal constant, which is equal to 0.37. The oxidation number V_i of the atom i is simply the algebraic sum of these 'v' values of all the bonds around the atom i, following equation

$$\sum v_{ij} = V_i \quad \dots(2)$$

This V_i is known as the BVS of the i th atom. Thus if R_{ij} is known for a particular bond type, the BVS can be calculated from the crystallographically determined d_{ij} values. The R_{ij} parameters reported by two groups of authors are used in the present calculations. $R_{ij}(\text{OK/B})$ is defined as ⁶:

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

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 $R_{ij} = r_i + r_j - (c_i c_j r_i r_j)$ and if $i = j$ then $f = 0$. $R_{ij}(\text{B/OK})$ values reported in references⁴, have also been used in the present calculations. In the case of mixed ligand complexes involving nickel-dithiocarbamates and phosphorous donor ligands, the BVS values are higher than the expected formal

Table 1: Size parameters

Bond	$R_{ij}(\text{OK/B})$	$R_{ij}(\text{B/OK})$
Zn-S	2.08	2.09
Zn-N	1.77	1.77
Cd-S	2.28	2.29
Cd-N	1.96	1.96

Table 2: BVS values for [Zn(S₂CN(Me)ⁱPr)₂]

Bond	d_{ij}	$v_{ij}(\text{OK/B})$	$v_{ij}(\text{B/OK})$
Zn-S	2.339	0.497	0.511
Zn-S	2.432	0.387	0.387
Zn-S	2.334	0.503	0.517
Zn-S	2.902	0.109	0.112
Zn-S	2.365	0.468	0.475
	$V_i =$	1.964	2.002

Table 3: Bond Valence Sums for Zinc complexes

Compound	Coordination number	$V_i(\text{OK/B})$	$V_i(\text{B/OK})$
[Zn ₂ (C ₆ H ₁₂ NS ₂) ₄]	4 ^a	1.89	1.95
[Zn ₂ (C ₇ H ₁₄ NS ₂) ₄]	4 ^a	1.91	1.96
[Zn(S ₂ CN(Et)Ph) ₂] ₂	4 ^a	1.90	1.95
[Zn(S ₂ CN(ⁱ Pr) ₂] ₂	4 ^a	1.94	2.00
[Zn(S ₂ CN(CH ₂) ₄] ₂	4 ^a	1.90	1.95
[Zn(S ₂ CN(CH ₂) ₆] ₂	4 ^a	1.95	2.01
[Zn(S ₂ CN(Me)Et) ₂] ₂	4 ^a	1.94	2.00
[Zn(S ₂ CN(Me) ⁿ Pr) ₂] ₂	4 ^a	1.97	2.03
[Zn(S ₂ CN(Me) ⁱ Pr) ₂] ₂	4 ^a	1.96	2.00
[Zn(S ₂ CN(Me) ⁿ Bu) ₂] ₂	4 ^a	1.94	1.98
[Zn(S ₂ CN(Me)Ph) ₂] ₂	4 ^a	1.91	1.96
[Zn(S ₂ CN(Et) ⁱ Pr) ₂] ₂	4 ^a	1.89	1.95
[Zn(S ₂ CN(Me)Cy) ₂] ₂	4 ^a	1.96	2.02
[Zn(S ₂ CN(Et)Cy) ₂] ₂	4 ^a	1.92	1.97
[Zn(S ₂ CNCy) ₂] ₂	4 ^a	2.01	2.07
[Zn(S ₂ CN(Et) ₂ (C ₅ H ₅ N)]	5	1.95	1.99
[Zn(S ₂ CNMe) ₂ (C ₅ H ₁₁ N)]	5	1.82	1.85
[Zn(S ₂ CN(CH ₂) ₄) ₂ (2,2'-bipy)]	6	1.87	1.90
[Zn(S ₂ CN(Me)Cy) ₂ (2,2'-bipy)]	6	1.85	1.89
[Zn(S ₂ CN(CH ₂) ₄) ₂ (2,9-Me ₂ -1,10-Phen)]	6	2.00	2.03
[Zn(S ₂ CN(CH ₂) ₄) ₂ (4,7-Ph ₂ -1,10-Phen)]	6	1.92	1.96
[Zn(C ₉ H ₁₈ NS ₂) ₂ (1,10-Phen)]	6	1.84	1.87
[Zn ₂ (S ₂ CNEt) ₄ (trans-NC ₅ H ₄ C(H)=C(H)C ₅ H ₄ N)]	5	1.92	1.96
[Zn(S ₂ CN(Me) ⁱ Pr) ₂ (1,10-Phen)]	6	1.89	1.93

^a Actual coordination number is five including a long Zn-S bond.

oxidation state of +2 due to the back bonding effect associated with the Ni-P distance^{7,8}. But for the divalent zinc and cadmium dithiocarbamate complexes the BVS value results in excellent agreement with the formal oxidation state of the metal^{9,10}. In continuation of our interest in assigning oxidation states on metals in metal dithiocarbamate complexes, in this work the crystallographic distances for a series of zinc and cadmium complexes and their adducts have been collected from the literature and the formal oxidation state of the metal ion were assigned by using BVS method.

RESULTS AND DISCUSSION

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 zinc and cadmium complexes are given in Table 3 and 4.

By making use of two different sets of parameters such as $V_i(OK/B)$ and $V_i(B/OK)$ the bond valence sums are calculated. Results of the investigations clearly showed 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, $V_i(B/OK)$, shows better agreement than the former with respect to the formal oxidation state of the central ion. Therefore both the 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

Table 4: Bond Valence Sums for Cadmium complexes

Compound	Coordination Number	$V_i(OK/B)$	$V_i(B/OK)$
$[Cd(S_2CN(nPr)_2)_2]$	4 ^a	1.97	2.02
$[Cd(S_2CN('pr)_2)_2]$	4 ^a	2.04	2.09
$[Cd(S_2CN('Bu)_2)_2]$	4 ^a	2.02	2.07
$[Cd(S_2CN(Et)Cy)_2]$	4 ^a	2.01	2.07
$[Cd(S_2CNCy_2)_2]$	4 ^a	2.06	2.12
$[Cd(S_2CNEt_2)_2(2,2'-bipy)]$	6	1.97	2.01
$[Cd(S_2CNEt_2)_2(1,10-Phen)]$	6	2.04	2.07
$[Cd(S_2CNEt_2)_2(2,9-Me_2-1,10-Phen)]$	6	1.98	2.03
$[Cd_2(S_2CNEt_2)_4(trans-NC_5H_4C(H)=C(H)C_5H_4N)]$	5	2.00	2.04
$[Cd(S_2CN(Bz)_2)(C_5H_5N)]$	5	1.97	2.01
$[Cd\{S_2CN(Bz)(CH_2CH_2OH)\}_2(1,10-Phen)]$	6	2.08	2.11
$[Cd\{S_2CN(Et)Ph\}_2(2,2'-bipy)]$	6	2.00	2.04

^aActual coordination number is five including a long Cd-S bond.

$(CH_2)_4CNS_2^-$ = pyrrolidinedithiocarbamate anion, $C_6H_{12}NS_2^-$ = N-ethyl-N-isopropylidithiocarbamate anion, $S_2CNCy_2^-$ = N,N-dicyclohexyldithiocarbamate anion, $S_2CN(Et)Ph^-$ = N-ethyl-N-phenyl dithiocarbamate anion, $S_2CN(Et)_2^-$ = N,N-diethylidithiocarbamate anion, $S_2CN('Pr)_2^-$ = N,N-diisopropyl dithiocarbamate anion, $S_2CN(Me)'Pr^-$ = N-isopropyl-N-methylidithiocarbamate anion, $S_2CN(Me)Et^-$ = N-ethyl-N-methylidithiocarbamate anion, $C_7H_{14}NS_2^-$ = N-butyl-N-ethylidithiocarbamate anion, $S_2CN(Me)Bu^-$ = N-butyl-N-methylidithiocarbamate anion, $S_2CN(Me)Ph^-$ = N-methyl-N-phenylidithiocarbamate anion, $S_2CN(Me)Cy^-$ = N-cyclohexyl-N-methylidithiocarbamate anion, $S_2CN('Bu)_2^-$ = N,N-di-isobutyldithiocarbamate anion, $S_2CN(nPr)_2^-$ = di-n-propylidithiocarbamate anion, $S_2CN(Bz)_2^-$ = N,N-dibenzylidithiocarbamate anion, $S_2CN(Bz)(CH_2CH_2OH)^-$ = N-(2-hydroxyethyl)-N-benzyl dithiocarbamate anion, $S_2CN(Et)Cy^-$ = N-cyclohexyl-N-ethylidithiocarbamate anion, $S_2CN(Et)'Pr^-$ = N-isopropyl-N-ethylidithiocarbamate anion, $S_2CNMe_2^-$ = N,N-dimethylidithiocarbamate anion, $C_9H_{18}NS_2^-$ = N,N-di-n-butylidithiocarbamate anion, $(CH_2)_6CNS_2^-$ = hexamethylenedithiocarbamate anion, 2,2'bipy = 2,2'-bipyridine, $C_5H_{11}N$ = piperidine 1,10 - Phen = 1,10-phenanthroline, C_5H_5N = Pyridine, $NC_5H_4C(H)=C(H)C_5H_4N$ = bis(4-pyridyl)ethylene. The fragment C_3H_5 is $-CH_2C(H)=CH_2$, i.e. allyl.

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. Generally, the valence bond sums for the parent zinc dithiocarbamate complexes are greater than the sums of the adducts¹¹. In the case of the adducts, the Zn-S distances are longer than the Zn(dtc)₂ complexes due to the presence of an additional neutral ligand causes an increase of the Zn-S bond lengths. The increase in Zn-S distances in the adducts indicates the weakening of the bond and this is very well in keeping with the BVS values obtained in the earlier studies¹¹. In the present study also similar trends have been observed with respect to the Zn-S distances and BVS values. But, interestingly the bond valence sum value of [Zn(S₂CN(CH₂)₄)₂(2,9-Me₂-1,10-Phen)] adduct is significantly greater than the value of parent [Zn(S₂CN(CH₂)₄)₂]. The increase in BVS values can be ascribed to the decrease in Zn-N and Zn-S distances (which are significantly shorter than those observed in 4,7-Ph₂-1,10-Phenanthroline analogue and in other nitrogenous adducts) due to the effect of electron releasing methyl substituent on 1,10-phenanthroline.

In all the cadmium complexes, the BVS values have been found to be close to '2' irrespective of the coordination number, which confirm the valency of the cadmium in the complexes. It has already been reported¹¹ that in the case of the cadmium dithiocarbamate

complexes and their adducts no observable changes are seen in BVS values. Owing to the larger size of cadmium ion when compared with zinc ion, the Cd-S distances are not much affected by the change in coordination geometry from four coordination to five or six. 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, which 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 requirements of the metal ion".

CONCLUSIONS

The bond valence sum (BVS) model can be applied to determine compatibility between a given coordination model and a particular unknown oxidation state. This method is useful to assign the oxidation state of the metal ions in main group metal complexes. In this paper, BVS have been calculated for a series of Zn(II) and Cd(II) dithiocarbamate complexes and their adducts. The BVS analysis has confirmed the valency of the central metal to be 2.0 as expected. It is concluded that the formation of a complex of any metal ion with multidentate ligand represent a compromise between the steric interactions in the ligand and the steric and electronic requirements of the metal.

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