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Valence Bond Sum (VBS) Analysis on Bis(dithiocarbamato) Nickel (II) and Complexes with NiS_4 Chromophore

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ABSTRACT

The use of valence bond parameter (R_{ij}) values determined from homoleptic extended solids in the calculations of VBS for divalent zinc, cadmium and mercury metallo-organic compounds resulted in excellent agreement with the formal oxidation state of the metal. But for compounds which involve transition metal ions the calculated oxidation states always are far higher than their formal oxidation states. In this paper, the use of new valence bond parameter, {R_{ij}(T)}, for a series of parent bisdithiocarbamates of nickel(II) improved the VBS value tremendously and the formal oxidation state of nickel is observed to be close to 2.0

Key words: Dithiocarbamate, Ionic radii, Nickel(II), Valence Bond parameter.

INTRODUCTION

With traditional use of the valence bond sum (VBS) method, the oxidation state of a central atom can be determined if the bond valence parameter (R_{ij}) value and the lengths of the bonds from donor atoms to the central atom are known. The VBS can be extremely useful to all chemists in resolving conflicts regarding oxidation states or in evaluating the results of a crystal structure analysis. 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[2-4] 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 VBS calculations were made and results were published for a series of zinc,

Table 1: VBS values for $[Ni(C_7H_{12}NS_2)_2]$

Bond	d_{ij}	v_{ij}(OK/B)	v_{ij}(B/OK)	v_{ij}(T)
Ni-S	2.1964	0.688	0.655	0.496
Ni-S	2.1923	0.696	0.663	0.502
Ni-S	2.2009	0.680	0.647	0.490
Ni-S	2.1892	0.701	0.668	0.506
Vi =2.765		2.633	1.994	

Table 2: Valence Bond Sums for Nickel dithiocarbamate complexes

Compound	V_i(OK/B)	V_i(B/OK)	V_i(T)
$[Ni\{S_2CN(i-C_3H_7)_2\}_2]$	2.856	2.720	2.060
$[Ni\{S_2CN(n-C_4H_9)(C_2H_5)\}_2]$	2.700	2.572	1.948
$[Ni(C_7H_{12}NS_2)_2]$	2.765	2.633	1.994
$[Ni\{S_2CN(C_2H_4OH)_2\}_2]$	2.718	2.588	1.960
$[Ni\{S_2CN(i-C_4H_9)_2\}_2]$	2.725	2.596	1.965
$[Ni\{S_2CN(C_2H_5)_2\}_2]$	2.720	2.590	1.960
$[Ni\{S_2CN(C_4H_8O)_2\}_2]$	2.636	2.510	1.900
$[Ni\{S_2CN(CH_2CH_2NEt)_2\}_2]$	2.686	2.560	1.936
$[Ni(S_2CNC_3H_6C_6H_4)_2]$	2.704	2.574	1.950
$[Ni(S_2CNHC_{10}H_{15})_2]$	2.718	2.590	1.960
$[Ni\{S_2CN(CH_2CH_2OMe)_2\}_2]$	2.700	2.570	1.944
$[Ni(S_2CNC_5H_{10})_2]$	2.712	2.576	1.958
$[Ni(S_2CNH_2)_2]$	2.616	2.494	1.886
$[Ni(S_2CNHMe)_2]$	2.730	2.600	1.968
$[Ni\{S_2CN(n-C_3H_7)_2\}_2]$	2.704	2.574	1.948
$[Ni(S_2CNHMePh)_2]$	2.704	2.574	1.950
$[Ni\{S_2CN(CH_2)_4\}_2]$	2.682	2.554	1.934
$[Ni\{S_2CN(n-C_3H_7)(C_2H_4OH)\}_2]$	2.700	2.545	1.930
$[Ni(C_7H_{10}NS_2)_2]$	2.696	2.568	1.944
$[Ni(C_{10}H_{10}NOS_2)_2]$	2.722	2.592	1.962
$[Ni(C_{11}H_{22}NS_2)_2]$	2.782	2.708	2.050
$[Ni(C_{18}H_{34}NS_2)_2]$	2.686	2.556	1.936
$[Ni\{S_2CNH(n-C_3H_7)\}_2]$	2.716	2.586	1.958
$[Ni\{S_2CNH(i-C_3H_7)\}_2]$	2.768	2.636	1.996
$[Ni(C_{10}H_{10}NS_2)_2]$	3.140	2.992	2.266

The Crystal structure data of the complexes were obtained from the corresponding literature.

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

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

T = calculated by the method due to H. H. Thorp

$^-S_2CN(i-C_3H_7)_2$ = *N,N*-diisopropyldithiocarbamato anion, $^-S_2CN(n-C_4H_9)(C_2H_5)$ = N-ethyl-N-butyldithiocarbamate anion, $C_7H_{12}NS_2^-$= 4-methylpiperidine carbodithioato anion, $^-S_2CN(C_2H_4OH)_2$= *N,N*-di(2-hydroxyethyl)dithiocarbamate anion, $^-S_2CN(i-C_4H_9)_2$ = *N,N*-diisobutyldithiocarbamate anion, $^-S_2CN(C_2H_5)_2$ = *N,N*-diethyldithiocarbamate anion, $^-S_2CN(C_4H_8O)_2$ = 4-morpholinecarbodithioato anion, $^-S_2CN(CH_2CH_2NEt)_2$ = 2-diethylamino ethyldithiocarbamate anion, $^-S_2CNC_3H_6C_6H_4$ = 1,2,3,4-tetrahydroi soquinolinedithio carbamate anion, $^-S_2CNHC_{10}H_{15}$ = N-adamantyldithiocarbamate anion, $^-S_2CN(CH_2CH_2OMe)_2$= bis(2-methoxyethyl) dithiocarbamate anion, $^-S_2CNC_5H_{10}$ = piperdine carbodithioato anion, $^-S_2CNHMe$= methyldithiocarbamate anion, $^-S_2CN(n-C_3H_9)_2$= di-n-propyldithiocarbamate anion, $^-S_2CNHMePh$ = N-Methyl-N-phenyldithio carbamate anion, $^-S_2CN(CH_2)_4$ = Pyrrolidinedithio carbamate anion, $^-S_2CN(n-C_3H_7)(C_2H_4OH)$ = N-Propyl-*N*-(2-hydroxyethyl)dithiocarbamate anion, $C_{10}H_{10}NOS_2^-$ = N-acetyl-N-benzyldithiocarbamate anion, $C_7H_{10}NS_2^-$ = *N,N*-diallyldithiocarbamate anion, $C_{11}H_{22}NS_2^-$ = dipentyldithiocarbamate anion, $C_{18}H_{34}NS_2^-$ = N-ethyl-N-cyclohexyldithio carbamate anion, $^-S_2CNH(n-C_3H_7)$=N-Propyldithiocarbamate anion, $^-S_2CNH(i-C_3H_7)$=N-iso-propyldithio carbamate anion, $C_{10}H_{10}NS_2$ = 1,2,3,4-tetrahydroquinolinedith iocarbamate anion, cadmium and nickel dithiocarbamate complexes and their adducts[5-8]. The VBS investigations for divalent zinc and cadmium dithiocarbamte complexes resulted in excellent agreement with the formal oxidation state of the metal. But for the nickel complexes, involving nickel-dithioocarbamates and phosphorous donor ligands, the VBS values are higher than the expected formal oxidation state of +2. In continuation of our interest in VBS calculations on metal dithiocarbamate complexes, the present anlaysis was undertaken to improve the VBS tremendously on nickel(II)dithiocarbamates by using the new R_{ij}(T) parameter. For this analysis the crystallographic distances for a series of parent nickel dithiocarbamate complexes have been collected from the literature and the VBS results are reported in this paper.

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[7] $\Sigma v_{ij} = V_i$. 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. For inorganic compounds, including those of transition metals, the parameter B is commonly accepted[9-10] to have a value of 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 [9]:

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

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 $R_{ij} = r_i+r_j-(c_i,c_j,r_i,r_j)$ and if i = j then f = 0. R_{ij}(B/OK) values reported in references[7], have also been used in the present calculations.

RESULTS AND DISCUSSION

Valence bond parameters, R_{ij}, available in the literature[7,9] for Ni–S, Ni–N, Ni-P, Ni–O are obtained from a statistical consideration of a very large number of homoleptic extended solid[7]. Use of those R_{ij} values[7], for isolated independent molecules of metallo-organic nature yielded very high VBS values leading to erroneous conclusion. Use of R_{ij} values determined from homoleptic extended solids in the calculations of VBS for divalent zinc, cadmium and mercury metallo-organic compounds resulted in excellent agreement with the formal oxidation state of the metal[7,9]. The observation is a clear case of a more or less ionic interaction prevailing in metallo-organic compounds involving d^{10} metal ions.

For compounds which involve transition metal ions such as Mo, Mn, Cu, Fe, Ni the agreement of the calculated oxidation states always are far higher than their formal oxidation states[11-13]. The bond valence sums for metal ions in isolated independent metallo-organic molecules agreed well with their formal oxidation by the use of a new set of R_{ij} parameters[10,11]. H.Thorp reported a set of new optimized R_{ij}(T) parameters for Ni^{+2}-O, Ni^{+2}-S, Ni^{+2}-N along with other data derived from isolated model compounds involving such interactions. Use of the R_{ij}(T) parameters for the parent bisdithio carbamates of nickel(II) improved the VBS tremendously and the formal oxidation state of nickel is observed to be close to 2.0. Valence bond sums are calculated for a series of complexes by making use of three different sets of parameters such as V_i(OK/B), V_i(B/OK) and Vi(T) reported in this paper. The calculated R_{ij} parameters are 2.058 R_{ij}(OK/B), 2.04 R_{ij}(B/OK) and 1.937 R_{ij}(T). A representative calculation of VBS values and the valence bond sums (VBS) of nickel dithiocarbamate complexes are given in Table 1 and 2 respectively.

CONCLUSIONS

Valence bond sum (VBS) is used by many researchers to determine the oxidation state of metal ions in solids based on crystallographically determined metal-ligand bond distances. In the transition metal complexes the calculated oxidation states by using R_{ij}(OK/B) and R_{ij}(B/OK) are always far higher than their formal oxidation states. In order to improve the VBS tremendously on a series of nickel(II)dithiocarbamates a new valence bond parameter, R_{ij}(T), is introduced and the formal oxidation state of nickel is observed to be close to 2.0

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