International Journal of Applied Research

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Study on BiS (dithiocarbamate) Nickel (II) and Complexes with NiS₄ Chromophone

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Abstract
The fundamental objective in this paper is to the utilization of valence security boundary (R_{ij}) values decided from homoleptic broadened solids in the counts of VBS for divalent zinc. cadmium and mercury metallo-natural mixes brought about magnificent concurrence with the conventional oxidation condition of the metal. However, for mixes which include change metal particles the determined oxidation states consistently are far higher than their conventional oxidation states. In this paper, the utilization of new valence bond parameter,$\{R_{ij}(T)\}$, for a progression of parent bisdithiocarbamares of nickel(II) improved the VBS esteem enormously and the conventional oxidation condition of nickel is seen to be near 2.0

Keywords: BiS (dithiocarbamate) Nickel (II) and NiS4 Chromophone

Introduction
The scientist wishing to gauge an obscure bond length in an atomic or gem is defied with a scary cluster of covalent radii, ionic radii, metallic radii and so forth., from which to choose [1]. The bond valence method [2-4] has as of late had significant accomplishment in predicating and deciphering bond length in 'ionic solids'. As it very well may be applied to gauge the bond length, the other way around the entirety of these bond lengths should give data about the valence of the focal particle. Utilizing the crystallographic information announced by our exploration gathering, the VBS computations were made and result were distributed for a progression 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	

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Table 2: Valence Bond Sums for Nickel dithiocarbamate complexes

Compound	V₁(OK/B)	V₁(B/OK)	V₁(T)
[Ni{S₂CN(i-C₃H₇)₂}₂]	2.856	2.720	2.060
[Ni{S₂CN(n-C₄H₉)(C₂H₆)}₂]	2.700	2.572	1.948
[Ni(C₇H₁₂NS₂)₂]	2.765	2.633	1.994
[Ni{S₂CN(C₂H₄OH)₂}₂]	2.718	2.588	1.960
[Ni{S₂CN(i-C₄H₉)₂}₂]	2.725	2.596	1.965
[Ni{S₂CN(C₂H₆)₂}₂]	2.720	2.590	1.960
[Ni{S₂CN(C₄H₈O)₂}₂]	2.636	2.510	1.900
[Ni{S₂CN(CH₂CH₂NEt)₂}₂]	2.686	2.560	1.936
[Ni(S₂CNC₃H₆C₆H₄)₂]	2.704	2.574	1.950
[Ni(S₂CNHC₁₀H₁₅)₂]	2.718	2.590	1.960
[Ni{S₂CN(CH₂CH₂OMe)₂}₂]	2.700	2.570	1.944
[Ni(S₂CNC₅H₁₀)₂]	2.712	2.576	1.958
[Ni(S₂CNH₂)₂]	2.616	2.494	1.886
[Ni(S₂CNHMe)₂]	2.730	2.600	1.968
[Ni{S₂CN(n-C₃H₇)₂}₂]	2.704	2.574	1.948
[Ni(S₂CNHMePh)₂]	2.704	2.574	1.950
[Ni{S₂CN(CH₂)₄}₂]	2.682	2.554	1.934
[Ni{S₂CN(n-C₃H₇)(C₂H₄OH)}₂]	2.700	2.545	1.930
[Ni(C₇H₁₀NS₂)₂]	2.696	2.568	1.944
[Ni(C₁₀H₁₀NOS₂)₂]	2.722	2.592	1.962
[Ni(C₁₁H₂₂NS₂)₂]	2.782	2.708	2.050
[Ni(C₁₈H₃₄NS₂)₂]	2.686	2.456	1.936
[Ni{S₂CNH(n-C₃H₇)}₂]	2.716	2.585	1.958
[Ni{S₂CNH(i-C₃H₇)}₂]	2.768	2.636	1.996
[Ni{C₁₀H₁₀NS₂}₂]	3.140	2.992	2.266

The Crystal structure data of the complex 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

S₂CN(i-C₃H₇)₂= N,N- diisopropyldithiocarbamato anion, ⁻S₂CN(n-C₄H₉)(C₂H₅) = N-ethyl-N-butyldithiocarbamate anion, C₇H₁₂NS₂= 4-methylpiperidine carbodithioato anion, ⁻S₂CN (C₂H₄OH)₂= N,N-di(2-hydroxyyethyl) dithiocarbamate anion, ⁻S₂CN(i-C₄H9)₂= N,N-diisobutyldithiocarbamate anion, ⁻S₂CN(C₂H₅)₂= N,N-diethyldithiocarbamate anion, ⁻S₂Cn (C₄H₈O)₂= 4-mopholinecarbodithioato anion, ⁻S₂CN(CH₂CH₂NEt)₂= 2 diethylamino ethyldithiocarbamate anion, ⁻S₂CNC₃H₆C₆H₄= 1,2,3,4-tetrahydrol soquinolinedithio carbamate anion, ⁻S₂CNHC₁₀H₁₅=N-adamantyldithiocarbamate anion, ⁻S₂CN(CH₂CH₂ OMe)₂= bis(2-methoxyethyl) dithiocarbamate anion, ⁻S₂CNC₅H₁₀= piperdine carbodithioato anion, ⁻S₂CNHMe= methyldithiocarbamate anion, ⁻S₂CN(n-C₃H₉)₂= di-n-propyldithiocarbamate anion, ⁻S₂CNHMePh =N-Methyl-N-phenyldithio carbamate anion, ⁻S₂CN(CH₂)₄= Pyrrolidinedithio carbamate anion, ⁻S₂CN(n-C₃H₇)(C₂H₄OH)= N-Propyl-N-(2-hydroxyethyl) dithiocarbamate anion, C₁₀H₁₀NOS₂= N-acetyl-N-benzyldithiocarbamate anion, C₇H₁₀NS₂= N,N-diallydithiocarbamate anion, C₁₁H₁₂NS₂= dipentyldithiocarbamate anion, C₁₈H₃₄NS₂= N-ethyl-N-cyclohexyldithio carbamate anion, S₂CNH(n-C₃H₇)= N-Propyldithiocarbamate anion, ⁻S₂CNH(i-C₃H₇)=N-iso-propyldithio carbamate anion, C₁₀H₁₀NS₂=1,2,3,4-tetrahydroquinolinedith locarbamate anion, cadmium and nickel dithiocarbamate complexes and their adducts [5-8]. The VBS investigations for divalent zinc and cadmium dithiocarbamate 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 Rᵢⱼ(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_1 obeys[7] $\sum V_{ij}=V$. The most commonly adopted relationship for the variation of the bond length d_{ij} with valences 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} parameter reported by two groups of authors are used in the present calculations. $R_{ij}(OK/B)$ is defined as [9].

$$R_{ij} = r_i+r_j-[r_ir_j(\sqrt{c_i}-\sqrt{c_j})_2]/[c_ir_j+c_ir_j]$$

Where r_i and r_j are size parameters of the atom i and j involved in bonding and c_i, cc_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 reference [7], have also been used in the present calculations.

Result and discussion

Valence bond boundary, R_{ij} accessible in the literature [7, 9] for Ni-S, Ni-N, Ni-P, Ni-O are gotten from a measurable thought of countless homoleptic expanded solid[7]. Utilization of those R_{ij} values [7], for confined free particles of metallo-natural nature yielded high VBS esteems prompting mistaken end. Utilization of R_{ij} esteems decided from homoleptic expanded solides in the figurings of VBS for divalent zinc, cadmium and mercury metallo-natural mixes brought about magnificent concurrence with the proper oxidation condition of the metal [7-9]. The perception is an away from of a pretty much ionic association winning in metallo-natural mixes including d [10] metal particles.

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 parameters [10-11]. H. Thorp reported a set of new optimized R(T) parameters for Ni-²-O, Ni⁺²-S, Ni²-N along with other data derived from isolated model compounds involving such interaction. 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 $V_i(T)$ 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.

Conclusion

Valence bond whole (VBS) is utilized by numerous specialists to decide the oxidation condition of metal

particles in solids dependent on crystallographically determind metal-ligand bond separations. In the progress metal buildings the determined oxidation states utilizing R_{ij} (OK/B) and R_{ij}(B/OK) are consistently far higher than their conventional oxidation states. So as to improve the VBS colossally on a progression of nickel(II) dithiocarbamates another valence bond boundary, $R_{ij}(T)$ is presented and the proper oxidation condition of nickel is seen to be near 2.0

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