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VALENCE BOND SUMS IN COORDINATION CHEMISTRY: CALCULATION OF THE OXIDATION STATE OF NICKEL IN NiS_2P_2 CHROMOPHORES BY USING A NEW VALENCE BOND PARAMETER

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ABSTRACT

We have first used valence bond sum method to assign the oxidation state of metal centers in the divalent zinc and cadmium dithiocarbamate complexes and on their adducts. The investigations resulted in an excellent agreement with the formal oxidation state of metal ions in the dithiocarbamate complexes. However, a series of similar investigations on nickel mixed ligand complexes which involve nickel dithiocarbamates and phosphorus donors showed that the calculated oxidation states are far higher than the formal oxidation state of nickel. Hence in order to improve the oxidation state on nickel center, in this study, we report a new valence bond parameter for nickel-phosphorus bond as per the procedure described earlier. Using this improved valence bond parameter, we have calculated oxidations states for a series of NiS_2P_2 chromophoric complexes whose crystal structures have been reported earlier and the formal oxidation state of nickel is observed to be close to +2

Keywords*:* Oxidation state, Valence Bond Sums, Dithiocarbamate, Nickel, Phosphorus

INTRODUCTION

Metal complexes have attracted significant attention because they have tremendous potential application in biology and light emitting devices[1,2]. The use of the valence bond sum (VBS) method in understanding the bonding in metal complexes shows promise[3]. The relation between bond length and bond valence, being a measure of the chemical bond strength and the related valence sum rule, plays a special role in the studies of crystal structure in structural chemistry and atomic microenvironment in coordination chemistry. In a significant number of cases, the information based on VBS 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[4]. The valence bond method[5,6] 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. The VBS analysis based on the valence bond parameters, R_{ij}(OK/B), R_{ij}(B/OK) (calculated by the method of O' Keefe and Brese) resulted in an excellent agreement with the formal oxidation state of the metal in the divalent zinc and cadmium dithiocarbamte complexes[7-9]. But in the mixed ligand complexes involving nickel-dithiocarbamates and phosphorus ligands, the VBS values (oxidation states) are higher than the expected formal oxidation state of +2.[10,11]

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To improve the VBS tremendously on nickel center in the mixed ligand complexes, the present study is undertaken by using the improved $R_{ij}(T)$ parameter for Ni-P bond which is calculated as per the procedure described earlier by H.H.Thorp[12,13].

EXPERIMENTAL

VBS Method

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[14] $\Sigma v_{ij} = V_i$. 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 three groups of authors are used in the present calculations. R_{ij}(OK/B) is defined as[15]:

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

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. The calculations in the present analysis are based on the use of three R_{ij} parameters viz., R_{ij}(OK/B), R_{ij}(B/OK) and R_{ij}(T), (OK/B), (B/OK) and (T) refer to author initials who reported R_{ij} values for various M-X bonds[14,15].

RESULTS AND DISCUSSION

R_{ij} parameters available in the literature[14,15] for Ni–S, Ni–N, Ni–P, Ni–O are obtained from a statistical consideration of a very large number of homoleptic extended solid. Use of those R_{ij} values[14-16] for isolated independent molecules of metallo-organic nature yielded very high VBS values leading to an 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 an 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 V, the formal oxidation states always are far higher than their formal oxidation states[12,13]. The valence bond 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[12,13]. H. 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. The use of optimized $R_{ij}(T)$ parameter for Ni-S bond improved the VBS tremendously on the parent bisdithiocarbamates of nickel(II) and the formal oxidation state of nickel is observed to be close to 2.0 [17].

A complete survey of the literature till date reveals the fact that no further attempt has been made to provide a new set of improved R_{ij} parameters for Ni–P bond. In this paper, we report the new Rij parameter for Ni–P bond as per the procedure described earlier[12,13]. On the basis of the improved R_{ij} parameter, the VBS values are calculated for a number of complexes whose crystal structures have been reported earlier. The use of the new $R_{ij}(T)$ parameter for Ni–P bond improved the VBS significantly on the nickel center in NiS_2P_2chromophores. Valence bond parameter (R_{ij}) values for Ni-S, Ni-P bonds and a representative calculation of VBS are given in Table-1 and 2 respectively.

Table-1: Size parameters

Bond	R_{ij}(OK/B)	R_{ij}(B/OK)	R_{ij}(T)
Ni-P	2.128	2.17	1.973
Ni-S	2.058	2.04	1.937

The valence bond sums (VBS) of nickel complexes are given in Table-3. The VBS values are higher in chelated phosphine complexes compared to free phosphine analogs. The higher values observed support the fact that the Ni–P bonds are more covalent and the back bonding effects are highly pronounced. Interestingly, the VBS values are significantly greater in the case of 1,2-dppe and 1,3-dppp adducts, which can be attributed to the very strong covalent and the back bonding effects, resulting in a shorter Ni–P bond lengths[18-20], which reflect on the VBS values.

Table-2: VBS values for [Ni(4-mpipdtc)($PPh_3)_2$]$^+$

Bond	d_{ij}	V_{ij}(OK/B)	V_{ij}(B/OK)	R_{ij}(T)
Ni-P	2.2149	0.791	0.886	0.520
Ni-P	2.2333	0.752	0.843	0.495
Ni-S	2.1937	0.693	0.660	0.500
Ni-S	2.2272	0.633	0.603	0.456
	V =	2.869	2.992	1.971

The complex formation 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.[21] The valence bond sums (VBS) of the complexes[14] determined form the valence bond parameters[22] account for the valence of the central ion irrespective of the number of bonds and the strength of interactions.

Table-3: Valence Bond Sums for NiS_2P_2Chromophores

Compound	Vi(OK/B)	Vi(B/OK)	Vi(T)	Ref.
[Ni(nmedtc)($PPh_3)_2$]$^+$	2.933	2..811	1.930	18
[Ni(pipdtc)($PPh_3)_2$]$^+$	3.042	2.915	2.002	23
[Ni(padtc)($PPh_3)_2$]$^+$	2.938	2.903	1.994	24
[Ni(bz^{i}prdtc)($PPh_3)_2$]$^+$	3.152	3.019	2.072	25
[Ni(dedtc)($PPh_3)_2$]$^+$	3.023	2.895	1.987	26
[Ni(dipdtc)($PPh_3)_2$]$^+$	3.029	2.905	1.997	27
[Ni(dnpdtc)($PPh_3)_2$]$^+$	2.934	3.065	2.005	28
[Ni(bzmedtc)($PPh_3)_2$]$^+$	2.833	2.956	1.944	29
[Ni(4-mpipdtc)($PPh_3)_2$]$^+$	2.869	2.992	1.971	30
[Ni(nmedtc)(dppe)]$^+$	3.282	3.131	2.145	18
[Ni(nmedtc)(1,3-dppp)]$^+$	3.259	3.150	2.134	31
[Ni(pipdtc)(1,3-dppp)]$^+$	3.216	3.261	2.103	20
[Ni(pipdtc)(1,4-dppb)]$^+$	3.066	2.942	2.018	32
[Ni(padtc)(dppe)]$^+$	3.256	3.109	2.131	24
[Ni(dedtc)(dppe)]$^+$	3.167	3.302	2.169	33
[Ni(dedtc)(1,4-dppb)]$^+$	3.146	3.006	2.062	34
[Ni(mdtc)(dppe)]$^+$	3.316	3.162	2.199	19
[Ni(mdtc)(1,3-dppp)]$^+$	3.196	3.05	2.089	35
[Ni(mdtc)(1,4-dppb)]$^+$	3.104	2.967	2.035	35
[Ni(dipdtc)(dppe)]$^+$	3.358	3.204	2.194	27
[Ni(dipdtc)(1,3-dppp)]$^+$	3.245	3.188	2.093	20
[Ni(plddtc)(1,4-dppb)]$^+$	3.240	2.968	2.035	36
[Ni(dnpdtc)(dppe)]$^+$	3.160	3.312	2.128	28

nmedtc- = N-methyl, N-ethanoldithiocarbamate anion, pipdtc- = piperidinecarbodithioate anion, padtc- = N,N'-iminodiethylenebis(phthalimide)dithiocarbamate anion, bziprdtc- = benzylisopropyldithiocarbamate anion, dedtc- = diethyldithiocarbamate anion, dipdtc- = diisopropyldithiocarbamate anion, dnpdtc- = di-n-propyldithiocarbamate anion, bzmedtc- = N-benzyl,N-methyldithiocarbamateanion, 4-mpipdtc- = 4-methylpiperazinedithiocarbamate anion, plddtc- = pyrolidinedithiocarbamate anion, PPh_3 = triphenylphosphine, dppe = 1,2-bis(diphenylphosphino)ethane, 1,3-dppp = 1,3-bis(diphenylphosphino)propane, 1,4-dppb = 1,4-bis(diphenylphosphino)butane.

CONCLUSION

VBS values are far higher than the formal oxidation state of nickel on NiS_2P_2 chromphores always. In an attempt to improve the VBS tremendously a new valence bond parameter, R_{ij}(T), is introduced for Ni–P bond and VBS values are calculated for a series of NiS_2P_2 chromophores and the formal oxidation state of nickel is observed to be close to +2. However, VBS values are significantly greater in the case of

1,2-dppe and 1,3-dppp adducts because of very strong covalent and the back bonding effects of Ni–P bond, which reflects on the VBS values.

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REFERENCES

1. R. Mayildurai, G. Dhinakaran, S. Karthikeyan and R. Ashok Kumar, *Rasayan J. Chem*., **10**, 1242 (2017), **DOI:** 10.7324/RJC.2017.1041921
2. M. Vijayalakshmi, *Rasayan J. Chem.*, **11**, 857 (2018), **DOI:**10.31788/RJC.2018.1123033
3. V. Sidey and A. Shteyfan, *J. Physics and Chemistry of Solids*, **103**, 73 (2017), **DOI:** 10.1016/j.jpcs.2016.12.004
4. Pauling, *The Nature of Chemical Bonding,* 3rdedn., Cornell Ithaca, NY, (1960)
5. I. D. Brown, *Structure and Bonding in crystals*, M. O'Keeffe, A. Navrotsky, Eds., Vol. 2 Academic, NY, (1981)
6. M. O. Keeffe, *Structure and Bonding*, **71**, 162 (1989)
7. A. Manohar, K. Ramalingam, G. Bocelli and A. Cantoni, *Polish J. Chem*.,**75**, 147 (2001)
8. S. Thirumaran, K. Ramalingam and G. Bocelli, *Main Group Metal Chem*., **22**, 423 (1999),**DOI:** 10.1515/MGMC.1999.22.7.423
9. K. Karpagavel and A. Manohar, *Orient. J. Chem*., **30**, 879 (2014), **DOI:** 10.13005/ojc/300268
10. B. Arul Prakasam, K. Ramalingam, M.Saravanan, G. Bocelli and A. Cantoni, *Polyhedron*, **23**, 77 (2004), **DOI:** 10.1016/j.poly.2003.09.013
11. A. Manohar, K. Ramalingam, K.Karpagavel, and G.Bocelli, *Adv. Materials Res*., **584**, 84 (2012)
12. H. Holden Thorp, *Inorg. Chem*., **31**, 1585 (1992), **DOI:** 10.1021/ic00035a012
13. W. Liu and H. H. Thorp, *Inorg. Chem*., **92**, 4102 (1993), **DOI**: 10.1021/ic00071a023
14. N. E. Brese and M. O. Keeffe, *Acta Cryst*., **B47**, 192 (1991), **DOI:** 10.1107/S0108768190011041
15. N. K. Ray, L. Samuels and N. G. Pan, *J. Chem. Phys*., **70**, 3680 (1979)
16. I. D. Brown and D. Altermatt, *Acta Crystagr*., **B41**, 244 (1985), **DOI:** 10.1107/S0108768185002063
17. A. Manohar and K. Karpagavel, *Orient. J. Chem*., **30**, 351 (2014), **DOI:** 10.13005/ojc/300147
18. A. Manohar, K. Ramalingam, V. Venkatachalam , U. Casellato and R. Graziani, *Polyhedron*, **15**, 1971 (1997), **DOI:** 10.1016/S0277-5387(96)00532-3
19. R. Akilan, K. Sivakumar, V. Venkatachalam, K. Ramalingam, K. Chinnakali, and H. K. Fun, *Acta Crystallogr.*, **C51**, 368 (1995), **DOI:** 10.1107/S010827019401070X
20. A. Manohar, K. Ramalingam, R. Thiruneelakandan, G. Bocelli and L. Righi.*Z. Anorg. Allg.Chem*., **627**, 1103 (2001), **DOI:**10.1002/1521-3749(200105)627:5<1103::AID-ZAAC1103>3.0.CO;2-8
21. S. P. Summers, K. A. Abboud, S. R. Farrah and G. J. Palenik, *Inorg. Chem*., **33**, 88 (1994), **DOI:** 10.1021/ic00079a017
22. M. O' Keefe and N. E. Brese, *J. Am. Chem. Soc*., **113**, 3226 (1991), **DOI:** 10.1021/ja00009a002
23. V. Venkatachalam, K. Ramalingam, R. Akilan, K. Sivakumar, K. Chinnakali and H. K. Fun, *Polyhedron*, **15**, 1289 (1996), **DOI:** 10.1016/0277-5387(95)00377-0
24. V. Venkatachalam, K. Ramalingam, G. Bocelli, A. Cantoni, *Inorg. Chim. Acta*, **257**, 49 (1997), **DOI:** 10.1016/S0020-1693(96)05447-3
25. R. Pastorek, J. Kamenicek, M. Pavilicek, J. Husarek, Z. Sindelar and Z. Zak, *Polish J. Chem*., **76**, 1545 (2002)
26. K. Ramalingam, G. Aravamudan and M. Seshasayee, *Inorg. Chem. Acta*, **128**, 231(1987), **DOI:** 10.1016/S0020-1693(00)86550-0
27. V. Venkatachalam, K. Ramalingam, T.C.W. Mak and L. B. Cheng, *Polyhedron*,**15**, 1295 (1996), **DOI**: doi.org/10.1016/0277-5387(95)00376-2
28. B. Arul Prakasam, K. Ramalingam, M. Saravanan, G. Bocelli and A. Cantoni, *Polyhedron,* **23**, 77 (2004), **DOI:** 10.1016/j.poly.2003.09.013

29. Z. Travnicek, R. Pastorek, P. Starha, I. Popa and V. Slovak, *Z. Anorg. Allg. Chem.*, **636**, 1557 (2010), **DOI:** 10.1002/zaac.201000091
30. B. Arul Prakasam, K. Ramalingam, R. Baskaran, G. Bocelli and A. Cantoni, *Polyhedron*, **26**, 1133 (2007), **DOI:** 10.1016/j.poly.2006.10.006
31. A. Manohar, K. Ramalingam, R. Thiruneelakandan, G. Bocelli andL. Righi, *Z. Anorg. Allg.Chem.*, **632**, 461 (2006), **DOI:** 10.1002/zaac.200500282
32. R. Thiruneelakandan, K. Ramalingam, A. Manohar, G. Bocelli and L. Righi,*Z. Anorg. Allg.Chem.*, **628**, 685 (2002), **DOI:**10.1002/1521-3749(200203)628:3<685::AID-ZAAC685>3.0.CO;2-D
33. G. Exarchos, S. D. Robinson and J. W. Steed, *Polyhedron,* **20**, 2951 (2001), **DOI:** 10.1016/S0277-5387(01)00885-3
34. K. Ramalingam, O. Bin Shawkataly, H. K. Fun and A. R. Ibrahim, *Acta Crystallogr.*,**C54**, 1223 (1998), **DOI:** 10.1107/S0108270198001917
35. A. Manohar, K. Ramalingam, G. Bocelli and L. Righi L. *Inorg. Chim. Acta*,**314**, 172 (2001), **DOI:** 10.1016/S0020-1693(00)00293-0
36. R. Pastorek, Z. Travnfcek, P. Ptosek, F. Brezina, J. Marek, Z. Sindelar and Z. Zak, *J. Coord. Chem.*, **44**, 247 (1998), **DOI:** 10.1080/00958979808023077

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