BOND VALENCE SUM ANALYSIS (BVS) OF METAL LIGAND BOND LENGTHS IN SOME Zn(II), Cd(II) DITHIOCARBAMATE COMPLEXES AND THEIR ADDUCTS

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Abstract: Bond valence sums have been calculated for a series of Zn(II), Cd(II) dithiocarbamate complexes and their adducts. Values calculated from crystallographic distances predict the correct oxidation state of the metal centre in a wide range of structural types. The BVS analysis for the bisdithiocarbamates of zinc, cadmium and their adducts has confirmed the valency of the central metal to be 2.0 as expected. In the case of zincdithiocarbamate complexes, the valence bond sums are in general greater than the sums for the adducts. The lower BVS values in the case of adducts are due to the change in coordination geometry from tetrahedral to octahedral. But in the case of Cadmium dithiocarbamate complexes and their adducts no observable changes are seen in VBS values. Relatively larger size of cadmium ion compared to zinc ion, alleviates the strain involved in the transformation from tetrahedral to octahedral geometry.

INTRODUCTION

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 [2,3] 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 the bond lengths should give information about the valence of the central ion. In the present study, the BVS method is applied to complexes of zinc and cadmium dithiocarbamates to estimate the effective valences of the metal ions from the bond lengths reported from their crystal structures.

The BVS 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 [4]

$$\sum_j v_{ij} = V_i$$

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. Two R_{ij} parameters are used in the present calculations viz., R_{ij} (OK/B) and R_{ij} (B/OK) which are reported by Bresse and O'Keeffe[4,5] respectively. R_{ij} (OK/B) is defined as [5],

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

where r_i and r_j are size parameters of the atoms 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 R_{ij} (B/OK) values reported in reference [4] have been used in the calculations. The R_{ij} (B/OK) values were deduced from the structural data directly. Similar data reported by Brown and Altermatt [6] did not include the R_{ij} values for Zn - S, Zn - N and Cd - N bonds. Hence 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)

The formation of a complex 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 [7]. The bond valence sums (BVS) of the complexes [4] determined from the bond valance parameters [8] account for the valence of the central ion irrespective of the number of bonds and the strength of interactions.

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 for $[Zn(S_2CNMe_2)_2]$ are given in Table 1 and 2 respectively. The Bond valence sums (BVS) of various complexes are given in Table 3. and 4. The BVS values for zinc and cadmium adducts and bis dithiocarbamates are also compared with those whose strucures have been reported in the literature.

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
Zn - O	1.63	1.70
Zn - I	2.38	2.36
Cd - S	2.28	2.29
Cd - N	1.96	1.96
Cd - I	2.57	2.57

TABLE 2. BVS values for $[Zn(S_2CNMe_2)_2]$

Bonds	d_{ij}	v_{ij} (OK/B)	v_{ij} (B/OK)
Zn - S	2.312	0.534	0.549
Zn - S	2.333	0.505	0.519
Zn - S	2.373	0.453	0.465
Zn - S	2.429	0.389	0.400
Zn - S	3.036	0.075	0.078
	V_i =	1.956	2.011

TABLE 3. Bond Valence sums for zinc complexes

Compound	Coordination number	V_i(OK/B)	V_i(B/OK)	Ref.
$[Zn(S_2CNMe_2)_2]$	4	1.96	2.01	9
$[Zn(S_2CNEt_2)_2]$	4	1.94	1.99	10
$[Zn(S_2CNMe_2)(C_7H_4NS_2)_2]^-$	4	1.91	1.94	11
$[Zn(deadtc)_2]$	4	1.88	1.93	12
$[Zn(bipiptds)I_2]$	4	2.00	1.96	13
$[Zn(S_2CNMe_2)py]$	5	1.94	1.98	14
$[Zn(S_2CNMe_2)(\mu\text{-}OCOMe)]^-$	5	1.83	1.95	15
$[Zn(pipdtc)_2(bipy)]$	6	1.85	1.89	16
$[Zn(mdtc)_2(bipy)]$	6	1.84	1.88	17

TABLE 4. Bond Valence sums for cadmium complexes

Compound	Coordination number	V_i(OK/B)	V_i(B/OK)	Ref.
$[Cd(S_2CNEt_2)_2]$	4	2.03	2.09	18
$[Cd(S_2CNC_6H_{12})_2]$	4	1.98	2.04	19
$[Cd(deadtc)_2]$	4	1.97	2.02	20
$[Cd(bipiptds)I_2]$	4	2.14	2.16	13
$[Cd(S_2COEt)_2(1,10\text{-phen})]$	6	1.97	2.00	21
$[Cd(S_2CSBu)_2(bipy)]$	6	2.02	2.05	22
$[Cd(pipdtc)_2(1,10\text{-phen})]$	6	2.00	2.03	23
$[Cd(pipdtc)_2(bipy)]$	6	2.03	2.07	23
$[Cd(mdtc)_2(1,10\text{-phen})]$	6	2.00	2.03	24

The Vi(OK/B) and Vi(B/OK) values for the zinc complexes are 1.90±0.05 and 1.96±0.04 respectively. Of the two sums, Vi(B/OK) is very close to 2.0. In the case of the parent, zinc dithiocarbamate complexes the valence bond sums are in general greater than the sums for the adducts. The values can be assumed to be close to 2.0 without any serious mistake because the BVS values are based on different bond distances which have uncertainities indicated by esd's.[25] Therefore both the BVS values (Vi(OK/B) and Vi(B/OK)) are close to 2.0 indicating the valence of the zinc in the complexes. Change in coordination number and change 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. The Zn-S distances in the adducts are longer than the $Zn(dtc)_2$ complexes. 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 present study.

Similarly for the cadmium complexes, of the two BVS values, Vi(B/OK) (2.01±0.05) is close to 2.0 rather than Vi(OK/B) (1.96± 0.04). In all the cadmium complexes, whether four coordinated or six coordinated, the BVS has been found to be close 2.0. Once again this confirms the valency of the cadmium in the complexes to be 2.0. The observed valency of the zinc and cadmium ions in many of the adducts have been found to be supported by a few representative investigations using XPS and CV recently[16,17,23].

The BVS analysis for the bisdithiocarbamates of zinc and cadmium and their adducts has confirmed the valency of the central metal to be 2.0 as expected. Besides that, this indirectly proves the correctness of the crystal structures determined in the present study [6].

REFERENCES

1. L.Pauling, The Nature of Chemical Bond, 3rd edn., Cornell Ithaca, New York, 1960.
2. I.D.Brown, Structure and Bonding in Crystals, M.O'Keeffe, A.Noworotsky, Eds., Vol.2 Academic, New York, 1981.
3. M.O'Keeffe, *Structure and Bonding* 1989, **71**, 162.
4. N.E.Brese and M.O'Keeffe, *Acta Crystallogr.*, 1991, **B47**, 192.
5. N.K.Ray, L.Samuels and N.G.Pan, *J. Chem. Phys.*, 1979, **70**, 3680.
6. I.D.Brown and D.Altermatt, *Acta Crystallogr.*, 1985, **B41**, 244.
7. S.P.Summers, K.A.Abboud, S.R.Farrah and G.J.Palenik, *Inorg, Chem.*, 1994, **33**, 88.
8. M.O'Keefe and N.E.Brese, *J. Am. Chem. Soc.*, 1991, **113**, 3226.
9. H.P.Klug, *Acta Crystallogr.*, 1966, **21**, 536.
10. M.Bonamico, G.Mazzone, A.Vaciago and L.Zambonelli, *Acta Crystallogr.*, 1965, **19**, 898.
11. J.A.McCleverty, N.J.Morrison, N.Spencer, C.C.Ashworth, N.A.Bailey, M.R.Johnson, J.M.A.Smith, B.A.Tabbiner and C.R.Taylor, *J. Chem. Soc., Dalton Trans.*, 1980, 1945.
12. S.Thirumaran, V.Venkatachalam, A.Manohar, K.Ramalingam, G.Bocelli and A.Cantoni, *J. Coord. Chem.*, 1998, **44**,281.
13. S.Thirumaran, K.Ramalingam, G.Bocelli and A.Cantoni, unpublished results.
14. K.A.Fraser and M.M.Harding, *Acta Crystallogr.*, 1967, **22**,75.
15. J.A.McCleverty, N.Spencer, N.A.Bailey and S.L.Shackleton, *J. Chem. Soc., Dalton Trans.*, 1980, 1939.
16. S.Thirumaran, K.Ramalingam, G.Bocelli and A.Cantoni, *Polyhedron*, in press.
17. S.Thirumaran, K.Ramalingam, G.Bocelli and A.Cantoni, unpublished results.
18. A.Domenicano, L.Torelli, A.Vaciago and L.Zambonelli, *J. Chem. Soc. A,* 1968, 1351.
19. V.M.Agre and E.A.Shugam, *Sov. Phys. Crystallogr.*, 1972, **17**, 256.
20. S.Thirumaran, A.Manohar, K.Ramalingam and Babu Varheese, unpublished results.
21. C.L.Raston and A.H.White, *Aust. J. Chem.*, 1976, **29**, 739.
22. S.J.Black, F.W.B.Eingtein, P.C.Hayes, R.Kwrar and D.G.Tuck, *Inorg. Chem.*, 1986, **25**, 4181.
23. S.Thirumaran, K.Ramalingam, G.Bocelli and A.Cantoni, unpublished results.
24. S.Thirumaran, K.Ramalingam, G.Bocelli and A.Cantoni, unpublished results.
25. M.Holden Thorp, *Inorg. Chem.*, 1992, **51**, 1505.

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