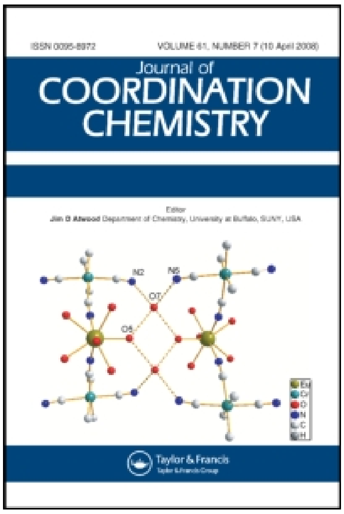

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ON THE COORDINATION IN METAL SACCHARINATES. IMPLICATIONS FOR BOND-ORDER MODELS OF METAL - LIGAND BINDING

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ON THE COORDINATION IN METAL SACCHARINATES. IMPLICATIONS FOR BOND-ORDER MODELS OF METAL–LIGAND BINDING

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The structures of saccharinates retrieved from the Cambridge Structural Database were used to discuss the coordination properties of deprotonated saccharin. The series of the first-row metal(II) saccharinato isomorphs and of triphenylstannyl saccharinates were analyzed within the bond valence model (BVM). The "relative radius" parameter of the saccharinato ligand for the $M(Ow)_4(Nsac)_2$ type of coordination was estimated (1.424 Å) from correlation of the metal–N(saccharinato) distances with the Shannon-Prewitt ionic radii.

Making use of the exponential bond distance-bond order (BDBO) relation of Pauling within the BVM, ligand-specific mean bond order sums (MBOS) were recently derived for several ligands. Coupled with the coordination number (CN), they are predictive for the metal–ligand bond lengths. Using parameterized power function instead of the exponential form of the BDBO relation, a new set of MBOS's is derived here: isothiocyanate 2.56 ± 0.06; pyridine 1.84 ± 0.16; imidazole 2.02 ± 0.12; chloride 2.05 ± 0.10; water 1.54 ± 0.03. The two sets of MBOS values can be used to predict the metal–ligand distances nearly equally well, showing that the distances are solely predetermined by the MBOS and CN values, independently of the particular form of BDBO relation used.

Keywords: Bond length; Bond order; Bond valence model; Coordination; Saccharinates

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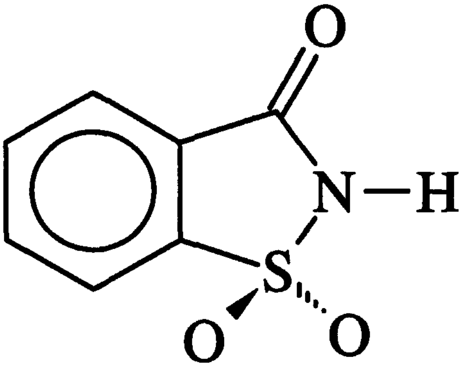
INTRODUCTION

The interest in the structural properties of the salts and complexes of saccharin (1,2-benzisothiazole-3(2*H*)-one 1,1-dioxide), commonly used artificial sweetener, has initially arisen from its potential pathogenic action on humans. The proximity of three different functional groups within the sulfoimide part (Scheme 1) and the versatility of the coordination modes of its nitration have later favored this compound as a model system for more fundamental structural studies. Our recent CSD survey of structures containing unsubstituted deprotonated saccharin [1] showed correlation between the distortions of the saccharinato five-membered ring and the respective metal–saccharinato distances. Individual discussions of saccharinato structures have regularly included comparison among related compounds; however, except for qualitative considerations of several copper(II) saccharinates [2], no systematic study on the coordination in saccharinates exists.

Some trends concerning the coordination number (CN), coordination geometry around the metal center and the metal–saccharinato distances can be expected from the structurally characterized mercury(II) saccharinates (Tab. I). Despite that (except for Hg(sac)$_2$) the compounds comprise varying secondary ligand and along with what is intuitively expected, generally *larger* CN corresponds with *longer* metal–N(saccharinato) distances. A question thus arises if one could predetermine the metal–N(saccharinato) distances solely from the CN and eventually other characteristic quantities for a particular metal–N(saccharinato) bond. Making use of the bond distance-bond order (BDBO) technique and the Pauling [3] relation within the bond valence model (BVM), in a recent study See *et al.* [4] have shown



SCHEME 1 Structural formula of saccharin.

TABLE I Coordination in mercury(II) saccharinates

	Compound				
	$Hg(sac)_2$ [26]	*HgCl(sac)* [36]	*$[Hg(bpy)(sac)_2]$* [37]	*$[HgCl(py)(sac)]_2$* [38]	*$[Hg(py)_2(sac)_2]$** [39]
Coordination geometry	digonal	digonal	tetrahedral	tetrahedral	tetrahedral
Coordination number	2	2	4	4	4
d(Hg–N(sac))/Å	2.04 (2) 2.05 (2) 2.03 (1) 2.06 (1)	2.021 (8)	2.141 (4) 2.120 (4)	2.106 (7)	2.156 (24) 2.148 (22)

* Further refinement of the data in progress.

that foreknowing the CN (within the inherent flexibility of the values of the metal–ligand distances), the metal–ligand bond lengths can be indeed estimated from the mean bond order sum (MBOS) at a certain metal center. Within that survey MBOS's that are ligand-specific for several common ligands were derived.

The accumulation and availability of structural data of saccharinates enabled us to undertake more systematic study of their coordination characteristics. The first aim of the present work was to estimate the bond orders and MBOS's of the saccharinato ligands at several metal(II) centers. From the saccharinato structures retrieved from the Cambridge Structural Database (CSD), two representative series of compounds were studied in more detail: the one consisted of isomorphous first-transition row and Cd metal(II) saccharinates hexahydrates (Series 1), and the second consisted of *O*-adducts of triphenylstannyl saccharinate (Series 2). In addition to the exponential BDBO function, we employed accordingly parameterized power form of the BDBO relationship. The second goal thus was to assess the two principal forms of BDBO relationship and the ligand-specific MBOS's for several common ligands towards their predictive power of the mean metal–ligand distances.

Collection, Selection and Compiling of the Data

The CSD data used in the present analysis were extracted from the hits retrieved in course of the former study of the saccharinato five-membered ring geometry [1]. The cut-criteria used for data collection are summarized in Table II. Four structures recently determined by us were added to the 44 hits retrieved from the CSD. Of this data set, the structures containing solely ionic deprotonated saccharin residues according to several structural criteria

TABLE II Selection and retrieval criteria for the Cambridge Crystallographic Database Survey

Selection criterion	
Saccharinato ligands/ions	Unsubstituted
R value	< 0.070
Temperature of data collection	Room and low
Multiple data sets with different *R*	The one with lowest *R* was included
Multiple data sets collected at different temperatures	The room-temperature one included
Neutron data	Excluded

(the original structure description, comparison of the metal–N(saccharinato) distances with the sums of the respective radii, results from IR, NMR, conductivity investigations, *etc.*) [1] were omitted.[1] In order to avoid any erroneous data, wherever possible, the values used in the analysis were compared with those contained in the respective original publications.

RESULTS AND DISCUSSION

General Considerations

In the solid state, deprotonated saccharin prefers coordination over the ionic form [1]. From the structures featuring coordinated saccharin, most abundant are the saccharinato complexes of Sn(II) (7), Cu(II) (7), Hg(II) (4) and Cr (4). With relatively large Lewis bases, the mixed Cu(II) complexes are mostly five-coordinated (KEXVAK, VOGRIS, YISNET, $[Cu(C_5H_5N)_2(sac)_2(H_2O)]$)[2], while smaller ligands (H_2O) yield octahedral coordination (ZZZFQQ11). The formation of a binuclear pattern, on the other hand, may result in *pseudo*-tetrahedral coordination (KIGBEH). The metal atom in the Hg(II) saccharinates is either diagonally or more probably tetrahedrally coordinated (Tab. I).

The unrestricted set of crystallographic data (including saccharinates with both non-coordinated and coordinated saccharin) allows discussion of some structural similarities among saccharinates. The octahedral coordination involving saccharin and water results in formation of rather relaxed structures with octahedral coordination, such as the isomorphous M(II) saccharinates (M = V, Cr, Mn, Fe, Co, Ni, Cu, Zn and Cd). Other, relatively

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[1] The 2,2′-bipyridine adduct of Cu(II) saccharinate is dihydrate (VOGRIS) rather than trihydrate (JITCOE) [5].

[2] Explanation of the refcodes used throughout the text is given in the Appendix.

small ligands (*e.g.*, NH_3) could probably yield similar series of octahedral isomorphs, $[Cd(NH_3)_4(sac)_2]$ (ZENFUT). Enlargement of the secondary ligand introduces variances in the coordination type. Thus, while the imidazole saccharinates $[M(C_3N_2H_4)_4(H_2O)_2](sac)_2$ of Mn, Fe, Co and Ni [6-8] are isomorphous, the Cu [9], Zn [8] and Cd [10] compounds have different structures. Similarly, the pyridine saccharinates $[M(H_2O)_4(C_5H_5N)_2](sac)_2 \cdot 4H_2O$ of Fe, Co and Ni form an isomorphous triad [11, 12], contrary to the Cu [13], Cd [12] and Zn [14] compounds. There are spectroscopic [15] and structural [16] evidence about isomorphism of the Co, Ni and Zn 2,2′-bipyridine complexes $[M(C_{10}N_2H_8)_2(sac)(H_2O)](sac)$, but the corresponding Cu [5] and Cd [17] adducts feature distinctively different structures.

Series 1: Isomorphous M(II) Saccharinates $[M(H_2O)_4(sac)_2] \cdot 2H_2O$ (M = V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Cd)

A well-known advantage of using the bond orders over the raw bond distances is that they can clearly afford more direct comparison among bonds between various atoms, the distances themselves being dependent on the type of the bonded atoms. The "traditional" BDBO expression was the one given by Pauling (Eq. (1)):

$$bo_{ij} = \exp[(d_{1,ij} - d_{ij})/k] \tag{1}$$

In Eq. (1), bo_{ij} is the bond order between the atoms i and j, d_{ij} and $d_{1,ij}$ are the bond distance and the single bond expectation distance between the atoms, respectively, and k is a constant originally set to $\{k\} = 0.31$ [3], but later corrected to 0.37 (*e.g.*, Ref. [6]), as we use it in this study. The values of $d_{1,ij}$, the meaning of which are considered to be solid-state single bond expectation distances, were calculated using the empirical expression (Eq. (2)) and the parameter values (r_i, r_j, c_i, c_j) reported by O'Keeffe and Brese [18]:

$$d_{1,ij} = r_i + r_j - [r_i r_j (c_i^{0.5} - c_j^{0.5})^2]/(c_i r_i + c_j r_j) \tag{2}$$

As noted by Cotton *et al.* [19], the crystal and molecular structure of the octahedral saccharinates of first transition row elements and Cd(II) of general formula $[M(H_2O)_4(sac)_2] \cdot 2H_2O$ (M = V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Cd) is exceptional for its flexibility, allowing relatively large variation of the cationic size without being collapsed. The isomorphous series contains as many as nine members with full and accurate enough X-ray structural data for all its members available and thus represents a favorable probe to examine structural factors that influence the geometry of the saccharinato ligand [1]. Parts of this series were in fact used several times previously for structural studies (*e.g.*, to correlate the metal–ligand distances [20-22], the geometry of the saccharinato sulfobenzoimide ring or the initial dehydration temperatures [23] with the Shannon-Prewitt ionic radii [24]).

The results of the structural analysis of Series 1 are presented in Table III. Since the octahedral Cu(II) center is subject to strong d^9 Jahn–Teller distortion from the ideal octahedral arrangement [19], the bond orders corresponding to the deformed bonds (0.063 and 0.268 for Cu–O2w and M–Nsac, respectively) were scaled prior to their inclusion in Table III. The analogous effect at the Cr(II) center is less pronounced [19] and thus no correction was applied in this case. If by the use of the BDBO technique the effect of cation type could be really eliminated, than the bond order sums within the series should be leveled and, according to the principal understanding of BVM, their values should be set equal or close to 2. As can be seen from Table III this is indeed so for most of the members of the series. The BOS's at the +2 metal saccharinato centers with coordination $M(Ow)_4(Nsac)_2$ average to 1.93 ± 0.06 and therefore satisfactorily close to 2. This result justifies the correction made above to account for the Jahn–Teller distortion in the Cu(II) compound. The use of statistically derived empirical parameters (*via* the $d_{1,ij}$ values), experimental uncertainties (*via* the d_{ij} values) as well as the inherent variation in the distance values due to the solid packing factors [25] might be reasons for the discrepancy of the individual bond order sums and consequently of the MBOS from 2. The value of the M–Nsac bond order alone in the case of $M(Ow)_4(Nsac)_2$ coordination averaged over the nine metal centers is 0.373 ± 0.023.

The first question that evolved from the above analysis was whether the calculated M–Nsac bond orders are dependent on the corresponding M–Ow bond orders. In this case, the M–Nsac bond orders calculated from the corresponding distances (*bo*(M–Nsac) in Tab. III) were correlated with their "expectation values" (*bo*(M–Nsac)$_e$), *i.e.*, the difference between 2 (bond order sum expected from the BVM) and the sum of the M–Ow bond orders at each metal center. The resulting correlation, however, was quite poor ($r = 0.5$). Therefore, in the present case the M–Nsac and M–Ow bond orders can be considered independent variables.

The second question that arose was whether the M–N distances can be correlated with the corresponding ionic radii, which can furnish the approximate "relative radius" parameter (the M–N distance at which the

TABLE III Structural analysis of the data concerning the coordination in the compounds of type $[M(H_2O)_4(sac)_2] \cdot 2H_2O$ (M = V, Cr, Mn, Fe, Co, Ni, Cu, Zn and Cd)

	$d_{ij}/\text{Å}$		$d_{1,ij}/\text{Å}$		Bond order				
M	*M−Nsac*	*M−Ow*	*M−Nsac*	*M−O*	*M−O1w*	*M−O2w*	*M−Nsac*	*M−Nsac*†	*BOS*
V [19]	2.225 (2)	2.143 (2) 2.174 (2)	1.889	1.774	0.369	0.339	0.403	0.292	2.222
Cr [19]	2.196 (3)	2.048 (3) 2.396 (4)	1.850	1.737	0.431	0.168	0.393	0.401	1.984
Mn [40]	2.281 (1)	2.162 (1) 2.219 (2)	2.288	2.172	0.328	0.282	0.322	0.390	1.864
Fe [22]	2.235 (2)	2.099 (2) 2.159 (2)	2.331	2.216	0.383	0.326	0.358	0.291	2.134
Co [22]	2.200 (1)	2.060 (1) 2.124 (2)	2.395	2.281	0.358	0.301	0.330	0.341	1.978
Ni [22]	2.154 (1)	2.042 (1) 2.096 (2)	2.448	2.335	0.333	0.288	0.329	0.379	1.900
Cu [22]	2.061 (2)	1.956 (2) 2.489 (3)	2.448	2.335	0.267	0.126*	0.536*	0.670	1.858
Zn [21]	2.201 (2)	2.159 (2) 2.201 (2)	2.352	2.238	0.230	0.258	0.309	0.512	1.594
Cd [21]	2.323 (4)	2.279 (4) 2.342 (4)	2.137	2.018	0.308	0.260	0.374	0.432	1.884

* Scaled using factor 2.
† "Expectation values" (see text).

metal ionic radius is equal to 0 Å [4]) of the saccharinato ligand for the present coordination geometry. Plots of this type for some members of Series 1 were in fact presented in several occasions previously [20-22], but no discussions other than qualitative considerations of ligand-field theory trends and the distances in the V(II) compound were given. As can be noticed from Figure 1, after exclusion of the d(Cu−N) value to account for the Jahn−Teller distortion, reasonable ($r = 0.88$, adjusted $r^2 = 0.73$) linear correlation ($d(\mathrm{M-N})/\text{Å} = 0.613 \cdot r(\mathrm{M}^{2+})/\text{Å} + 1.741$) between the M−N(sac) distances and the ionic radii[3] was found. The far right-handed point in the plot on Figure 1 refers to the only second transition-elements row ion, Cd(II), which nevertheless follows the general trend. Much larger population of data used by See *et al.* [4] than the one in this study showed good linear correlation between the mean M−N distances for isothiocyanate, imidazole and pyridine, on the one hand, and the Shannon-Prewitt radii on the other. The "relative radius" of the saccharinato ligand (1.424 Å) identified as the y-axis intercept of the slope 1.00 line through the point representing the mean M−N distance and ionic radius is expectedly larger than those estimated [4] for the relatively smaller N-donor ligands: pyridine (1.304 Å), imidazole (1.280 Å) and isothiocyanate (1.215 Å)[4]. However, one should bear in mind that the value for the saccharinato ligand is derived from a very limited number of data and that the coordination around the

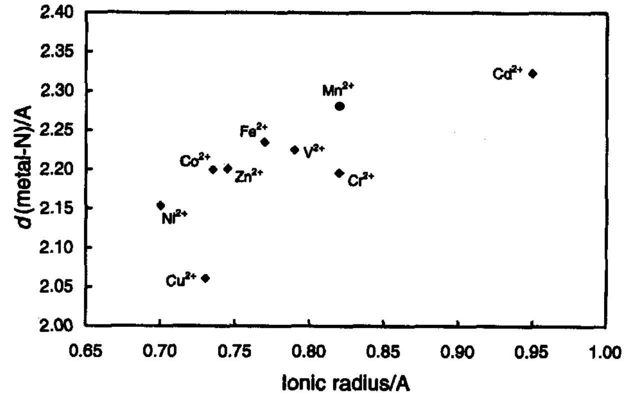

FIGURE 1 Plot of the M−N(saccharinato) distances in the isomorphous $[M(H_2O)_4(sac)_2] \cdot 2H_2O$ *vs*. Shannon−Prewitt radii.

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[3] The reasons to employ values for the ionic radii listed by Shannon−Prewitt were based solely on their wide use.

[4] The straight line discussed here does not represent a regression line.

metal includes four more molecules of water, which could lead to severe discrepancy of this parameter from its real value. The plot in Figure 1 moreover shows that averaging metal–bond distances instead of the respective bond orders over several metal centers (even if these were of the same oxidation state and in structurally related compounds) would be an oversimplification.

In order to inspect the influence of the crystal packing on the variation of the metal–ligand distances we searched for saccharinato compounds that contain chemically equal but crystallographically non-equivalent structural units with coordinated saccharin. The single case so-far known is mercury(II) saccharinate (MGSACC10) [26] comprising two structurally different $Hg(sac)_2$ moieties. The structural data of this compound, however, were not refined enough to obtain very accurate estimation (Tab. I); the approximate variation in the distance being of the order of several hundreds of an Å.

Series 2: Triphenylstannyl Saccharinates

The availability of full structural data for triphenyltin(II) saccharinate (SOXDAK) [27] and six of its *O*-adducts [28-33] (Tab. IV) is advantageous to examine trends concerning the structure of a saccharinato ligand [1]. Since the organometallic (Sn–C) and coordination (Sn–Nsac, Sn–O) bonds have clearly dissimilar nature and thus the common application of the classical BDBO model might be disputable, the use of Series 2 is restricted here to variation of the Sn–N(sac) bond order upon change of one ligand (the *O*-donor base) within the SnC_3NsacO coordination geometry.

Excluding the parent compound (SOXDAK), the sum of the Sn–Nsac and Sn–O bond orders is found to be relatively constant (0.94 ± 0.03, Tab. IV) and nearly uniform over various Sn–C bond orders. The bond orders of the coordination ligands, therefore, are practically complementary to each other and behave independently from those of the phenyl ligands, which justifies their individual treatment.

Ligand-specific Bond Order Sums

In addition to Eq. (1), several other schemes were proposed to derive the bond orders from the corresponding bond distances. The least-squares fit of interatomic distances to the integer bond orders results was modeled with a power function [34] of the corresponding bond distances rather than by an

TABLE IV Metal–ligand distances (Å) and the corresponding bond orders of the triphenylstannyl saccharinates

						Bond orders				
Refcode	*Sn–Nsac*	*Sn–C1*	*Sn–C2*	*Sn–C3*	*Sn–O*	*Sn–Nsac*	*Sn–C1*	*Sn–C2*	*Sn–C3*	*Sn–O*
SOXDAK	2.167	2.118	2.124	2.127		0.766	1.082	1.064	1.056	
KASYEI	2.24	2.111	2.12	2.128	2.394	0.629	1.102	1.076	1.053	0.307
KICXAV	2.243	2.132	2.15	2.129	2.409	0.624	1.042	0.992	1.050	0.295
VIHCEU	2.242	2.12	2.126	2.122	2.403	0.626	1.076	1.059	1.070	0.300
VUJXUT	2.237	2.137	2.125	2.129	2.412	0.634	1.028	1.061	1.050	0.293
	2.253	2.147	2.141	2.147	2.376	0.607	1.000	1.017	1.000	0.322
YELMIL	2.265	2.123	2.117	2.128	2.319	0.588	1.067	1.085	1.053	0.376
HIGWAV	2.236	2.137	2.132	2.134	2.341	0.636	1.028	1.042	1.036	0.354

exponential one. The rearranged relation is Eq. (3):

$$bo_{\mathrm{ij}} = [(\{d_{1,\mathrm{ij}}\} - \{d_{\mathrm{ij}}\})/x + 1]^{y} \tag{3}$$

The values of x and y are usually between 0.60 and 1.06, and 0.41 and 0.25, respectively.[5]

Whether through parameterization or by inclusion of the single-bond distance expectation values, the BDBO relations (Eqs. (1), (3) and (4)) make use of parameters that are characteristic for a specific pair of atoms. Therefore they tend to eliminate the differences of the atoms of various bonds and to enable comparison among these bonds.

The use of various BDBO schemes, however, would lead to various values of the ligand-specific MBOS's. Bearing in mind the conclusions of See *et al.* [4] derived by utilizing Eq. (1), one could reinforce assessment of MBOS values obtained using various BDBO expressions towards their predictive power for the metal–ligand distances within a larger population of determined structures. Since it is clear that such analysis cannot be performed within a relatively small set of data as the saccharinates, we used the results for the mean bond distances obtained by See *et al.*, to test Eqs. (1) and (3) towards their modeling ability of metal–ligand distances.[6] Contrary to bonds between electronegative atoms, the values for the parameters x and y used previously ($x = 0.78$, $y = 0.33$, [34]) did not represent satisfactorily the expected bond orders of the metal–ligand distances. Since the primary goal here was assessment of the applicability of the two forms of BDBO relation rather than parameterization of Eq. (3), we corrected the parameter values of Eq. (3) to meet the present data. The value of x was kept at 0.78, while y was calculated as an average[7] (over the three possible CN's, 4, 5 and 6) of the values that would give the best fits for the respective mean bond lengths to the bond orders expected from the BVM (*i.e.*, for the +2 ions used in this study: $2/6 = 0.333$ for CN 6; $2/5 = 0.400$ for CN 5; $2/4 = 0.500$ for CN 4). The value of y estimated this way amounted 1.80.

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[5] For the bond order between electronegative elements, Gordy [35] proposed that the bond orders are proportional to the reciprocal of the squared distance between the atoms (Eq. (4)):

$$bo_{\mathrm{ij}} = a d_{\mathrm{ij}}^{-2} - b \tag{4}$$

The characteristics of the bonding atoms are incorporated through two characteristic parameters (a and b in Eq. (4)). Later Paolini [22] tabulated improved values of the parameters and compared the Eqs. (1), (3) and (4) for the case of C–C bonds.

[6] Owing to the lack of parameter values for the bonds considered, Eq. (4) was not included in the analysis.

[7] The data for the $CuCl_6$ ligands along the z axis were excluded.

Following the approach of See *et al.* [4], the mean bond order sums for each metal–ligand pair at various coordination geometries were calculated (Tab. V) as product of the mean bond orders, obtained from including the mean metal–ligand distances into Eq. (3), and the corresponding CN's.

TABLE V Bond order sums calculated using functions of a power[*] and exponential[†] form

	Ion					
	Mn^{2+}	*Fe*$^{2+}$	*Co*$^{2+}$	*Ni*$^{2+}$	*Cu*$^{2+}$	*Zn*$^{2+}$
$d_{1,ij}$(M−N)/Å[‡]	1.86	1.82	1.79	1.74	1.76	1.77
$d_{1,ij}$(M−Cl)/Å[‡]	2.12	2.08	2.05	2.01	2.03	2.04
$d_{1,ij}$(M−O)/Å[‡]	1.75	1.71	1.68	1.63	1.65	1.66

CN	*Coordination*	*Bond order sums*[¶]					
isothiocyanate							
6	octahedral	2.66 **2.49**		2.73 **2.59**	2.46 **2.23**		
5	trigonal bipyramidal					2.75 **2.74**	2.55 **2.49**
4	tetrahedral			2.60 **2.65**	2.47 **2.50**		2.44 **2.47**
4	square planar				2.90 **3.00**	2.40 **2.43**	
pyridine							
6	octahedral		1.95 **1.52**	2.08 **1.71**	2.04 **1.65**		
4	tetrahedral						1.81 **1.71**
4	square planar				2.55 **2.59**	1.93 **1.86**	
imidazole							
6	octahedral		2.13 **1.77**	2.14 **1.79**	2.13 **1.77**		
5	square pyramidal					2.19 **2.03**	
4	tetrahedral						2.14 **2.12**
4	square planar				2.60 **2.65**	2.07 **2.04**	
chloride							
6	octahedral	2.15 **1.81**	2.11 **1.75**	1.89 **1.43**	2.16 **2.85**[§]		
5	square pyramidal					2.23 **2.07**	
4	tetrahedral (only MCl$_4$)	2.09 **2.06**	2.10 **2.08**	2.16 **2.15**	2.04 **2.00**	2.17 **2.16**	2.17 **2.15**
4	square planar					1.98 **1.93**	

TABLE V (Continued)

CN	*Coordination*	*Bond order sums*[¶]					
water							
6	octahedral	1.91 **1.45**	1.97 **1.54**	1.99 **1.58**	1.91 **1.46**	1.91 **1.57**	1.89 **1.43**
5	square pyramidal					1.88 **1.61**	
5	trigonal bipyramidal						1.87 **1.60**
4	tetrahedral						1.63 **1.47**
4	square planar					1.83 **1.74**	

[*] $bo_{ij} = [(\{d_{1,ij}\} - \{d_{ij}\})/0.78 + 1]^{1.80}$ (Distances in Å).
[†] $bo_{ij} = \exp[(\{d_{1,ij}\} - \{d_{ij}\})/0.37]$ (Distances in Å).
[‡] As used by See *et al.* [4].
[¶] Plain numbers are derived with the exponential, bold type numbers with the power relation.
[§] Only the value for the equatorial distances was used; see the text.

Due to the geometrical nonequivalence of the sites, the bonds in the five-coordinated complexes were treated separately and the bond order sums were calculated as $4bo_{\text{basal}}+bo_{\text{apical}}$ for square pyramidal geometry and $3bo_{\text{equatorial}}+2bo_{\text{axial}}$ for the trigonal bipyramidal geometry. To account for the Jahn–Teller deformations of the $Cu(H_2O)_6$ octahedron, the bond order sum was obtained as $4bo_{xy}+2bo_z$. However, Eq. (3) with the present arguments applied to the mean Cu–Cl bond length along the y axis for the case of the octahedral $CuCl_6$ produced an imaginary result, and in this case only the mean bond length of the shorter bond was used (*i.e.*, all bonds were treated equal to 2.294 Å). This is not the most convenient, but anyhow useful way to obtain this particular mean bond order sum. The ligand-specific mean bond order sums for isothiocyanate, imidazole, chloride, pyridine and water were then recalculated and are presented in Table VI together with the original values [4]. As can be inferred from there, the values for isothiocyanate, pyridine, imidazole and chloride obtained from the same set of data (mean bond distances and $d_{i,ij}$'s) and the BDBO relations given by Eqs. (1) and (3) are insignificantly different, with the largest discrepancy of only 0.8σ in case of imidazole. Generally, the mean

TABLE VI Mean bond order sums and their standard errors derived by the exponential [4] and power BDBO relation

	Ligand				
	Isothiocyanate	*Pyridine*	*Imidazole*	*Chloride*	*Water*
See *et al.* [4]	2.56 ± 0.13	1.95 ± 0.10	2.13 ± 0.04	2.12 ± 0.07	1.88 ± 0.10
This study	2.56 ± 0.06	1.84 ± 0.16	2.02 ± 0.12	2.05 ± 0.10	1.54 ± 0.03

bond order sums produced by the parameterized exponential relation may be somewhat lower than their original values. Difference of about 3σ is found for the smallest neutral ligand–water. This is expected from the understanding that for relatively small bond lengths (such as those of the metal–Ow bonds), the exponential BDBO function will normally produce larger bond order values. This significant difference additionally contrasts water as the only O-donating ligand to the N-ligands and chloride ion treated in this study. Close resemblance between the values of individual and mean bond order sums obtained by the two different BDBO functions (Tabs. V and VI) leads to conclusions of more general significance for the bond-order-based models. Namely, implementation of the concept of ligand-specificity of mean border sums withdrawn from a representative amount of experimental data within the "classical" BDBO model (based on the exponential Pauling relationship) into a substantially distinct BDBO relation produces nearly the same result. These assumptions show that to a large extent the basic structural concepts elucidated by use of various BDBO schemes are independent of the particular method of calculation. Various BDBO expressions are aimed to eliminate the nature of the bonded atoms in modeling purposes rather than to produce absolute values for bond orders as representation of the respective bonds.

In order to estimate the predictive power of the present ligand-specific bond order sums, correlation was attempted between the mean ligand distances used to derive their values and the ones obtained after their use, foreknowing the CN. Eq. (3) was therefore transformed to give Eqs. (5) and (6), expressing the bond distances:

$$\{d_{\mathrm{ij}}\} = \{d_{1,\mathrm{ij}}\} - 0.78(bo_{\mathrm{ij}}^{1/1.80} - 1) \tag{5}$$

$$\{d_{\mathrm{ij}}\} = \{d_{1,\mathrm{ij}}\} - 0.78[(\mathrm{MBOS/CN})^{1/1.80} - 1] \tag{6}$$

Excluding the five coordinate and Jahn–Teller six-coordinate Cu(II) compounds to account for the consequences of the approximations made, a good correlation is observed between the predicted and the observed M–ligand distances (Fig. 2). The value of the correlation coefficient R was 0.984 (R squared 0.968, adjusted[8] R squared 0.967), while the mean deviation from a linear correlation was found to be 0.020 Å. This latter value is very close to 0.017 Å found by See *et al.* [4], and shows that the metal–ligand

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[8] Adjusted $R^2 = 1 - $[(Residual sum of squares)/(Degrees of freedom)]/[(Total sum of squares)/(Degrees of freedom)].

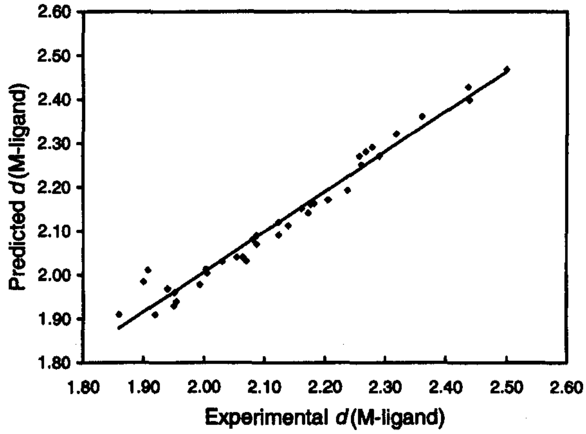

FIGURE 2 Plot of M-ligand distances observed experimentally *vs.* those predicted by the power form of the BDBO relation (Å).

distances can be modeled nearly equally well with the power form of the BDBO relation. The uncertainty of about 0.02 Å is in fact *a priori* expected from the variations in the structural parameters due to the effects of the crystal environment [25].

The implications from the consistency between the mean bond order sums and the mean bond lengths derived by the exponential and the power form of the BDBO relation are more general. Namely, the above conclusions justify the concept of ligand-specificity of MBOS's, regardless to the particular form of BDBO relation. The fact that the metal-ligand distances are determined by the CN and the nature of the ligand and the metal ion is in fact solely a natural consequence of geometrical factors, rather than to a particular scheme used to bring the various metal–ligand distances to the same scale.

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APPENDIX

Refcodes and empirical formulae of saccharinates mentioned in the text.

Refcode	*Formula*[¶]
HIGWAV	$Ph_3Sn(PPh_3)(sac)$
KASYEI	$Sn(C_6H_5)_3(sac) \cdot EtOH$
KEXVAK	$[CuL(sac)](H_2O)$
KICXAV	$Sn(C_6H_5)_3(sac)(OCHCOO)$
KIGBEH	$[Cu_2(C_3N_2H_4)_4(sac)_4]$
MGSACC10	$Hg(sac)_2$
SOXDAK	$[(C_6H_5)_3Sn(sac)]$
VIHCEU	$Sn(C_6H_5)_3(sac)(OCH_2N(CH_3)_2)$
VOGRIS	$[Cu(bpy)_2(sac)](sac) \cdot 2H_2O$
VUJXUT	$[Sn_2(C_6H_5)_6L'_2]$
YELMIL	$[Sn(C_6H_5)_3L''(sac)]$
YISNET	$[Cu(phen)_2(sac)](sac) \cdot 2H_2O$
ZENFUT	$[Cd(NH_3)_4(sac)_2]$
ZZZFQQ11	$[Cu(H_2O)_4(sac)_2] \cdot 2H_2O$

[¶] Acronyms denote: sac – saccharinato ligand or an ion; bpy – 2,2′-bipyridine; phen – 1,10-phenthroline; L, L′, L″ – N-donor ligands.