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Theoretical and Molecular Modelling Studies on Organic Transition Metal Complexes, II. Calculation of the Stability Constants of Bidentate Ligands in Relation to the *Irving-Williams* Order [1]

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The bidentate chelates of the transition elements Mn to Zn with salicylaldoxime, 8-hydroxyquinoline and 8-mercaptoquinoline have been constructed using molecular graphics and the stability constants derived from the calculated reaction enthalpies using an extended CNDO/2 method. The results generally follow the *Irving-Williams* order except for the mercaptoquinoline where large entropy effects are known to be present experimentally. The influence of substituents on the stability constant of salicylaldoxime is reflected in the calculated value particularly for electron-withdrawing groups.

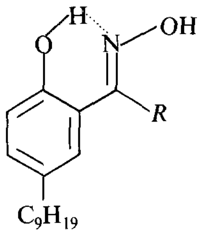
(Keywords: Molecular modelling; Stability; Transition metals; Chelates)

Theoretische und Molekülmodellierungs-Studien von organischen Übergangsmetallkomplexen, 2. Mitt.: Berechnung der Stabilitätskonstanten von zweizähnigen Liganden in Relation zur Irving-Williams-Ordnung

Die zweizähnigen Chelate der Übergangsmetalle Mn bis Zn mit Salicylaldoxim, 8-Hydroxychinolin und 8-Mercaptochinolin wurden unter Verwendung von molekulargraphischen Methoden und den Stabilitätskonstanten aus den mittels einer erweiterten CNDO/2-Methode ermittelten Reaktionsenthalpien konstruiert. Die Ergebnisse folgen generell der *Irving-Williams*-Ordnung, mit Ausnahme von 8-Mercaptochinolin, von dem bekannt ist, daß experimentell große Entropieeffekte auftreten. Der Einfluß von Substituenten auf die Stabilitätskonstanten der Salicylaldoximkomplexe spiegelt sich besonders für elektronenabziehende Gruppen in den berechneten Werten deutlich wider.

Introduction

There is growing interest in the design of organic ligands for the selective solvent extraction of a given transition metal from aqueous solutions containing mixtures of other elements. Both alkylated salicylaldoximes (**1 a**) and *o*-hydroxybenzophenone oximes (**1 b**) have been used successfully for the commercial recovery of copper from dilute acidic leach solutions by countercurrent extraction into hydrocarbon solvents [2]. The resulting solvent soluble copper bis(chelates) yield pure aqueous copper solutions on contact with strong sulphuric acid. Related extractants such as alkylated 8-hydroxyquinoline (**2**) have also been studied extensively for copper [3] hydrometallurgy, but are generally less effective. In all cases, long complex branched chain alkyl groups, such as nonyl or dodecyl groups, are present in the ligands to facilitate the solubility of the metal bis(chelate) and prevent its crystallisation during the extraction process [5].



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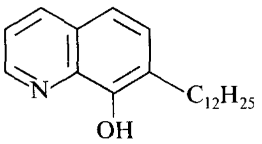
a $R = H$
b $R = C_6H_5$



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Although copper and many other transition metals are generally octahedrally coordinated in water alone, little information is available on the structure of the alkylated bis(chelates) in commercial hydrocarbon solvents or indeed in mixed aqueous ethers. However, the structures of simple alkylated bis(chelates) such as the bis(2-methyl-8-quinolinolato) complexes of cobalt, nickel, copper, and zinc are thought to be dimeric in chloroform with one molecule placed above the other in approximately a five coordinated geometry [6] which may loosely resemble that found in the crystalline state. Similar results have been reported for the unsubstituted 8-hydroxyquinoline complex of zinc in chloroform [7, 8], and it seems unlikely that the alkylated transition metal complexes are simple solvated species in non-polar solvents.

In principle, the design of ligands for the solvent extraction of transition metals can be accomplished using molecular graphics and theoretical calculations given that some structural information is available. Furthermore, provided it can be shown that the formation of structurally related chelates derived from bidentate aromatic or heterocyclic ligands either occurs with a constant entropy term or the entropy of the process shows an approximately linear relationship with the enthalpy [1], then the calculation of the free energy and hence the stability constant can be achieved in principle by calculating the reaction enthalpy (ΔE) of the chelation

$$M^{2+} + 2L^{-} \rightleftharpoons ML_2$$

using the expression

$$\Delta E = E(ML_2) - E(M^{2+} + 2L^{-})$$
$$\Delta E \sim \Delta G = -RT\ln K$$

where E is the binding energy of the molecular components [1].

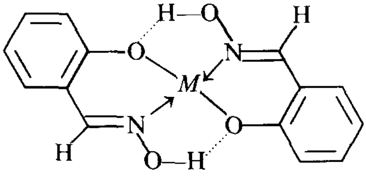
Calculations of this type using an extended CNDO/2 method have given satisfactory correlations between the ΔE values of a wide range of substituted copper bis(salicylaldehydes) and the experimental stability constant [1]. This method has now been applied to a series of bidentate ligands in an endeavour to predict the stability constants of transition metal complexes in non-polar solvents. Although there are data available on the effect of substituents and different transition metals on the stability constants of aromatic or heterocyclic ligands such as salicylaldoximes [9], catechols [10], 8-hydroxy- and 8-mercapto-quinolines [11], benzothiazoles [12], 1,2-diaminobenzenes [13], phenanthrolines [13], phenylanthranilic acids [14], phenylhydrazopyrazolines [15], salicylic acids [16], and phenols [17, 18], with a variety of transition metals in aqueous solvents, the structure of the complexes are not known.

In the present studies it has been assumed that the structure of the respective metal complex in hydrocarbon solution resembles that found in the crystalline state. Salicylaldoxime, 8-hydroxyquinoline and 8-mercaptoquinoline were selected for the studies reported here because the crystal structures of both the ligands and some complexes are known. It was anticipated that the extended CNDO/2 method with its careful transition metal parameterisation would distinguish not only the influence of substituents but also the effects of different transition metals and correctly predict the order of stability constants along the transition metal series which would be expected to follow that established in partially aqueous solvents such as 50 or 75% dioxan [12, 17] (the *Irving-Williams* order) [19].

Results and Discussion

Stability Constants of Metal Salicylaldoximes

Calculations were carried out on a range of unsubstituted metal salicylaldoximes (**3**) from Mn—Zn and substituted derivatives of Zn, Co and Ni. While the copper [20] and nickel [21] bis(complexes) are known to be square planar, no data are available on the remainder of the first transition metal series. However, in the related metal salicylaldimines (**4**), the copper and nickel complexes are also square planar [22], those of zinc [24] and cobalt [25] are distorted tetrahedra (or trigonal bipyramids), while the lower members of the series are generally polymeric with higher co-ordination numbers [22].



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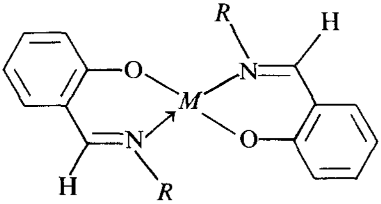

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For the purpose of the present studies, it has been assumed that the copper and nickel complexes are square planar while those of zinc, cobalt, iron and manganese are tetrahedral. The metal-oxygen and metal-nitrogen bond lengths adopted for the calculation of the copper and nickel oximes (**1**) were taken directly from the crystallographic data (Table 1); those for the zinc, cobalt, iron, and manganese oximes were derived from an analysis of the available crystallographic data on related systems.

Table 1. *Selected structural data for the bis(salicylaldimine) complexes of the transition metals*

Metal	*R*	*R*′	Average bond distances		*R*-Factor[a]	ESD[b]	Cambridge reference[c]
			M—O	*M*—N			
Cu	H	H	1.9305	1.9085	13.0	0	CUSAAI
	Me	H	1.9009	1.9891	8.0	0	MSACOP
	Et	H	1.8899	1.9560	10.3	3	CUESAL10
	Et	H	1.8876	2.0028	7.7	3	CUESAL02
	^{i}*Pr*	H	1.8777	1.9775	5.9	3	ISALCU01
	^{t}*Bu*	H	1.8973	1.9849	7.9	0	BSALCU10
	Cyclohexyl	H	1.8959	2.0344	3.7	1	CHSALC01
	Allyl	H	1.8758	2.0151	7.5	3	ALSACU10
	Ph	H	1.8776	1.9933	6.0	0	PSALCU
	OH	H	1.9147	1.9440	9.7	0	SALCOP
	OH	5-Cl	1.9082	1.9579	7.0	0	CSALCU
Ni	H	H	1.8403	1.8401	13.7	4	SALONI
	Me	H	1.8508	1.9188	2.6	1	MSLDNI10
	Et	H	1.8428	1.9245	14.0	3	ESALNI10
	^{i}*Pr*	H	1.8958	1.9707	6.0	0	ISALNI
	Cyclohexyl	H	1.9030	1.9949	5.4	1	BOLNEV
	Allyl	H	1.8436	1.9047	9.0	3	ASALNI10
	HO	H	1.8430	1.8555	14.0	3	NISALO
Zn	*Me*	H	1.9380	2.0070	4.8	1	SALEZN
Co	^{i}*Pr*	3-O*Me*	1.9072	1.9856	13.0	0	MXSPCO
Fe	^{n}*Pr*	H	1.8846	2.0949	11.6	4	CLFSAL10
Mn	Benzyl	H	1.8983	2.2013	5.2	2	BZSLMN

[a] *R*-Factor is a measure of the agreement between the structure as postulated relative to the diffractometer data as collected

[b] Estimated standard deviation in bond length between two heavy atoms. The values are: 0 = not assigned; 1 = 0.001–0.005 Å; 2 = 0.006–0.010 Å; 3 = 0.011–0.030 Å; 4 = 0.030 Å

[c] The names quoted are unique and taken from the Cambridge Structural Database System [35]

An examination of the data for substituted copper salicylaldimines generally chosen with low *R*-factors* except in those cases where only one structure is available (Table 1) shows that there is surprisingly little variation in the metal-oxygen bond length as the substituent, *R*, either increases in size along the series *R* = *Me*, *Et*, ^{i}*Pr*, ^{t}*Bu*, to cyclohexyl or is changed so that *R* = allyl, phenyl, or hydroxyl as in the oxime (**1**). The

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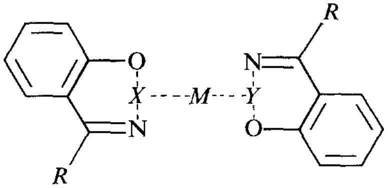
* See Table 1 for definition.

data for the unsubstituted complex (R = H) appears to be anomalous. A similar picture emerges for the corresponding nickel complexes, except in those cases where the substituent is fairly bulky such as the N-cyclohexyl derivative where the nickel-oxygen bond is significantly longer.

In contrast, the metal-nitrogen bond lengths are more sensitive, especially for the nickel complexes, and increase with an increase in the size of the substituent which now is attached directly to the nitrogen atom. An analysis of the data shows that the metal-nitrogen bond lengths in both the copper and nickel oximes (**1**) at 1.94 and 1.86 Å is some 97% of those found in the corresponding N-methylsalicylaldimines (**2**, $R = Me$) at 1.99 and 1.92 Å respectively.

The metal-nitrogen bond lengths for related N-alkylsalicylaldimine complexes of zinc and cobalt, are also known (Table 1) but no data is available for iron (II) or manganese (II) complexes in this series, although bond length data is available for iron (III) chloro-bis (N,N-propylsalicylaldimine) and manganese (III) tris (N-benzylsalicylaldimine). Bond length data for the calculation of unknown unknown bis-oximes (**1**, M = Zn, Co, Mn, Fe) were derived, therefore, from the above complexes by scaling the metal-nitrogen bond lengths by 0.97 and adopting the metal-oxygen bond lengths directly from the salicylaldimine structures without further modification in view of the very small variations observed between the bond lengths of the N-alkylsalicylaldimines and the salicylaldoximes of copper and nickel.

The geometry of the salicylaldoxime ring and the angles surrounding the metal atoms of all the complexes calculated in the present work were based on the known crystal structure of copper bis(salicylaldoxime) which is better resolved and more symmetrical than the corresponding nickel complex. While the square planar copper complex was calculated directly, the nickel complex was constructed from the copper complex by replacing the metal atom and decreasing both the metal-oxygen and metal-nitrogen bond lengths to the appropriate values using molecular graphics. A template for the tetrahedral complexes was generated by perpendicular rotation of one half of the molecule about points X and Y which were placed midway between the nitrogen and oxygen atoms of each half of the square planar copper complex as shown. The metal-nitrogen and metal-oxygen bond lengths were then adjusted to the selected values for the respective metals.



The calculated energies of the metal complexes, metal ions, and salicylaldoxime anion, are shown in Table 2. Because the structure of the iron and manganese complexes cannot be defined with any degree of certainty owing to the penta-co-ordinate and polymeric character of related complexes [22, 24], the results were not expected to correlate particularly well with the *Irving-Williams* order [19]. In the event the calculations give the following order of reaction enthalpies (ΔE):

$$Mn^{2+} < Fe^{2+} < Co^{2+} < Ni^{2+} < Cu^{2+} > Zn^{2+}$$

which is fully consistent with the stability constants experimentally determined in aqueous dioxan [9] except for the iron complex which appears to be anomalous since it conflicts with the known order of most iron complexes along the first transition metal series. The parameterisation scheme adopted for the transition metals at the CNDO/2 level, therefore, reproduces the expected order of stability constants.

Calculations were carried out also on the 5-methyl-, 5-chloro-, and 5-nitro-derivatives of the square planar nickel complex and tetrahedral cobalt and zinc complexes. In these cases, substituents were added to the respective square planar or tetrahedral template using standard bond lengths of 1.52 Å (*Ar*-CH_3), 1.71 Å (*Ar*-Cl), and 1.47 Å (*Ar*-NO_2). On the whole, the calculated results (Table 4) again correlate well with the experimental data in aqueous dioxan with the exception of the 5-methyl derivative of all three metal salicylaldoximes which give a smaller ΔE value than that expected. This ambiguity arises from the inherent approximation of the CNDO/2 method rather than the parameterisation adopted for the transition metals in view of similar trends obtained for the proton ionisation constants of both 3- and 5-methylsalicylaldehydes [1] and 5-methylsalicyldoxime (Table 2) where no metal is involved. Electron-withdrawing substituents present in the complexes reduce the stability constant and this is clearly reflected by the smaller binding energies obtained.

Stability Constants of 8-Hydroxy-(Oxine) and 8-Mercapto-quinolinates (Thiooxine)

Copper bis(8-hydroxyquinolinate) is square planar [26, 27, 28] but little data is available on other metals with the exception of zinc which forms either an octahedral complex with 8-hydroxyquinoline and water [29], manganese which forms an octahedral tris-complex, and iron which forms a mu-oxo-bis complex with 2-methyl-8-hydroxyquinoline [31]. The related 8-mercaptoquinoline complexes are square planar for copper, tetrahedral for zinc and cobalt, and may be either for nickel depending on the substituent pattern (see Table 4). The geometries of the bis-oxinates

Table 2. *Calculated binding energies and stability constants for metal bis(salicylaldoximes)*

Element	Type[a]	Bond distances (Å)		Binding energies (eV)			ΔE (eV)	log K (expt)[c]	log K (calc)[d]
		$M-O$	$M-N$	M^{2+}	Reactants[b]	Complex			
Zn	T	1.9380	1.9468	22.5560	− 426.0764	− 445.2689	− 19.1925	13.5 ± 0.2	15.30
Cu	SP	1.9147	1.9440	23.0212	− 425.6112	− 450.7179	− 25.1067	21.5 ± 0.2	20.02
Ni	SP	1.8430	1.8550	22.0013	− 426.6311	− 445.7834	− 19.1523	14.3 ± 0.2	15.27
Co	T	1.9072	1.9260	21.2167	− 427.4157	− 444.6898	− 17.1198	13.5 ± 0.1	13.65
Fe	T	1.8846	2.0321	20.6123	− 428.0201	− 442.6665	− 14.6464	16.73 ± 0.05	11.68
Mn	T	1.8983	2.1353	19.8164	− 428.8160	− 442.1315	− 13.3155	11.9 ± 0.2	10.62

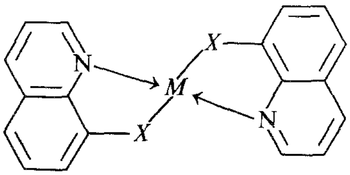
[a] T = tetrahedral conformation; SP = square planar conformation

[b] Binding energy of the salicylaldoxime anion = − 224.3162 (eV)

[c] Ref. [9]

[d] Derived from the best fit between experimental data in aqueous dioxan and calculated for the isolated chelate

adopted for calculation (**5**) were based on the symmetrical copper bisoxine [28] by adjustment of the metal-oxygen and metal-nitrogen bond lengths using molecular graphics to the values found in the nearest related structure. Because no data are available for nickel or cobalt, the bond lengths were derived from the copper complex by scaling the values with the relative ratios found for each metal in the salicylaldoxime complexes. The corresponding bond lengths for the zinc oxine were derived in the same way as the observed values are greater than expected because of the presence of two additional coordinating water molecules in the octahedral structures. Copper and nickel were calculated in the square planar conformation, while zinc, cobalt, iron, and manganese were constructed and calculated in the tetrahedral conformation using the same procedure as described for the salicylaldoximes. The results obtained are shown in Table 5 and it is clear that a good correlation is again observed with experimental data in 50% aqueous dioxan [11] with the copper complex showing the greatest stability and the manganese complex the least. The stability constant, and hence the free energy of the complexation reaction, is therefore dominated by the reaction enthalpy (see below).



5 $X = \mathrm{O}$
6 $X = \mathrm{S}$

The geometries of all the bis(8-mercaptoquinolinates) adopted for calculation (**6**) were derived from the symmetrical well-resolved structure of bis(5-methylthio-8-mercaptoquinolinato) copper(II) complex [32] by replacement of the 5-methylthio-substituent with hydrogen. The corresponding 7-methylthio-complex is better resolved [33], but this was not considered because of the possible distorting influence of the substituent adjacent to the site of complexation. The metal-sulphur and metal-nitrogen bond lengths for complexes of Ni, Zn and Co were adjusted to the values found in related structures (Table 4). Copper and nickel were calculated in the square planar conformation, while zinc and cobalt were constructed and calculated in the tetrahedral conformation again using the procedure described for the salicylaldoximes. Clearly, the conformation of the nickel complex is highly dependent on the substituent

Table 3. *Calculated binding energies and experimental pK*

Element	Substituent	Binding energy ($LH \rightleftharpoons L^- + H^+$)[c] (eV)			
		Oxime	Anion	Reactants	ΔE
Zn	None	-228.8023	-224.3162	-206.9364	21.8659
	5-Methyl	-262.8358	-258.3512	-240.9714	21.8644
	5-Chloro	-229.2732	-225.2735	-207.8937	21.3795
	5-Nitro	-262.1428	-258.6576	-241.2778	20.8650
Ni	None				
	5-Methyl				
	5-Chloro				
	5-Nitro				
Co	None				
	5-Methyl				
	5-Chloro				
	5-Nitro				

[a] Ref. [9]

[b] T = tetrahedral conformation; SP = square planar conformation

[c] Binding energy of H^+ = 17.3798 (eV)

pattern since the introduction of a substituent *ortho* to the nitrogen atom changes the thio-oxinate from a square planar to tetrahedral conformation.

The calculated results are shown in Table 6 where the order of calculated energies surprisingly decreases down the series Ni > Co > Cu > Zn in contrast to the experimental stability constants [34] in 50% aqueous dioxan which decrease in the order Cu > Co > Mn > Zn > Ni also in apparent conflict with the *Irving-Williams* order [19]. A possible explanation for the reversal of the usual order in the calculations may be attributed either to an inadequate parameterisation for the bonding parameters of the transition metals with the sulphur atom, or the selection of inaccurate geometries for the bis-thio-oxinates. However, it seems unlikely that the geometries are in error since the data adopted for both the square planar nickel and copper complexes which show reversed order are derived from several sources.

Predictions of the stability constant based on the calculated binding energy differences between the complex on the one hand and the reactants on the other are dependent on a reasonably constant entropy term. An *and log K values for substituted metal bis(salicylaldoximes)*

pK (expt)[a]	Binding energy ($M^{2+} + 2L^- \rightleftharpoons ML$) (eV)			$\log K$ (expt)[a]	Conformation[b]
	Reactants	Complex	ΔE		
10.70 ± 0.05	− 426.0764	− 445.2689	− 19.1925	13.5 ± 0.2	T
11.06 ± 0.05	− 494.1474	− 513.2233	− 19.0759	14.3 ± 0.2	T
10.25 ± 0.05	− 427.9910	− 446.2761	− 18.2851	11.6 ± 0.2	T
8.72 ± 0.05	− 494.7592	− 511.8897	− 17.1305	10.9 ± 0.1	T
	− 426.6311	− 445.7834	− 19.1523	14.3 ± 0.2	SP
	− 494.7011	− 513.7552	− 19.0541	14.7 ± 0.2	SP
	− 428.5457	− 446.7454	− 18.1997	13.7 ± 0.1	SP
	− 495.3139	− 512.3294	− 17.0155	13.8 ± 0.1	SP
	− 427.4157	− 444.6898	− 17.1198	13.5 ± 0.1	T
	− 495.4867	− 512.6235	− 17.1368	14.34 ± 0.2	T
	− 429.3303	− 445.3252	− 15.9949	13.3 ± 0.1	T
	− 496.0985	− 511.2249	− 15.1264	12.9 ± 0.2	T

analysis of experimental thermodynamic data for the mono- and bis-oxinates of the transition elements is shown in Table 7 where the values shown have been averaged from various sources [11]. While the entropy of chelation (ΔS_1) of the mono-oxinates is reasonably constant with the order of stability constants dominated by the enthalpy of chelation (ΔH_1), that for the bis-oxinates (ΔS_2) is more variable with the copper and zinc chelates showing higher than expected values. Overall, the order of stability constants for the bis-oxinates ($\log K^{\mathrm{tot}}$) is dependent mainly on the enthalpy of chelation (ΔH^{tot}), and the approach adopted in this work is therefore justified.

However, the entropy of chelation (ΔS_1) for the mono-thio-oxinate varies considerably depending on the transition metal in question, and the stability constant ($\log K_1$) is no longer proportional to the enthalpy of chelation (ΔH_1). No data is available for the thermodynamic properties of the bis-thio-oxinates though a comparison between the $\log K_1$ value [11] and the overall stability constant ($\log K^{\mathrm{tot}}$) [34] suggests that the latter is also strongly influenced by the entropy of chelation especially for the cobalt and nickel complexes which have much larger values than expected.

Table 4. *Selected structural data for substituted 8-hydroxyquinolinato- and 8-mercaptoquinolinato-complexes of the transition elements*

Metal	Substituent	X[a]	Mean bond distances		R-Factor[b]	ESD[b]	Cambridge reference[b]	Confor-mation
			$M-X$	$M-$N				
Ni	2-*Me*	S	2.2265	2.0812	17.0	0	MERQUI10	T
Ni	—	S	2.4036	2.0590	14.2	0	MEQUNI	SP
Ni	5-^{n}*Pr*S	S	2.2157	1.9532	9.5	0	PMQONI10	SP
Ni	2-*Me*	S	2.2283	2.0212	4.2	3	MERQUI01	T
Ni	2-^{i}*Pr*	S	2.2207	2.0295	6.0	3	ZZZAYJ20	T
Ni	5-^{n}*Pr*S	S	2.1947	1.9867	3.2	3	PMQONI20	SP
Cu	—	O	1.9304	1.9732	7.0	0	CUQUIN	SP
Cu	—	O	2.0408	1.9091	18.0	0	CUQUIN01	SP
Cu	—	O	1.9381	1.9826	18.0	0	CUQUIN13	SP
Cu	5-*Me*S	S	2.2781	2.0393	5.8	2	MEQUCU10	SP
Cu	7-*Me*S	S	2.2629	2.0324	2.9	2	COGMUG	SP
Cu	—	S	2.3065	2.0813	13.2	0	COGNAN	SP
Zn	—	O	2.0511	2.0735	22.6	4	ZNAHQU	O
Zn	—	O	2.0658	2.0983	13.0	0	ZNAHQU01	O
Zn	5-^{n}*Bu*S	S	2.2448	2.1019	12.0	4	BTSQZN10	T
Co	2-^{i}*Pr*	S	2.2410	2.0360	12.0	0	IMPQCO10	T
Mn	—	O	1.9147	2.1670	6.3	4	MNQOLH10	O
Mn	—	O	1.9134	2.1884	7.9	3	MNQOLM10	O
Fe	2-*Me*	O	1.9252	2.1848	12.6	3	MHQINF	TB

[a] X is the atom at the 8-position of the molecule

[b] See Table 1 for definitions

[c] T = tetrahedral; SP = square planar; O = octahedral; TB = trigonal bipyramid

It follows, therefore, that the calculated enthalpy results, ΔE, may be valid though clearly they cannot be used to deduce the stability constant.

It is concluded that a combination of molecular graphics and theoretical chemistry can be a powerful tool for the prediction of both reaction enthalpies and the stability constants of metal complexes. The good correlation obtained between the calculated stability constants and the experimental data in 50% aqueous dioxan for both the salicylaldoximes and oxine complexes suggests that solvation effects may be reasonably constant for square planar complexes.

Table 5. *Calculated binding energies and stability constants for metal bis(8-hydroxyquinolinates)*

Element	Type[a]	Bond distances (Å)		Binding energies (eV)			E (eV)	log K (expt)[c]	log K (calc)[d]
		$M-O$	$M-N$	M^{2+}	Reactants[b]	Complex			
Zn	T	1.9617	1.9854	22.5560	− 520.5438	− 536.2395	− 15.6957	18.15	19.39
Cu	SP	1.9381	1.9826	23.0212	− 520.0786	− 541.8781	− 21.7995	25.90	26.93
Ni	SP	1.8656	1.8918	22.0013	− 521.0985	− 537.4891	− 16.3906	20.27	20.25
Co	T	1.9305	1.9642	21.2167	− 521.8831	− 536.6859	− 14.8028	18.05	18.29
Fe	T	1.9252	2.1848	20.6123	− 522.4875	− 537.8470	− 15.3595	—	18.97
Mn	T	1.9141	2.1777	19.8164	− 523.2834	− 533.1337	− 9.8503	13.49	12.17

[a] T = tetrahedral conformation; SP = square planar conformation

[b] Binding energy of the 8-hydroxyquinoline anion = − 271.5499 (eV)

[c] Ref. [11]

[d] Derived from the best fit between experimental data in 50% aqueous dioxan and calculated results for the isolated chelate

Table 6. *Calculated binding energies and stability constants for metal bis(8-mercaptoquinolinates)*

Element	Type[a]	Bond distances (Å)		Binding energies (eV)			ΔE (eV)	$\log K$[c]
		$M-O$	$M-N$	M^{2+}	Reactants[b]	Complex		
Zn	T	2.4079	2.1683	22.5560	− 498.8220	− 536.8192	− 37.9972	25.7
Cu	SP	2.2781	2.0393	23.0212	− 498.3560	− 543.1676	− 44.8108	32.4
Ni	SP	2.1947	1.9867	22.0013	− 499.3767	− 546.3044	− 46.9277	25.2
Co	T	2.2410	2.0360	21.2167	− 500.1613	− 545.6552	− 45.8895	28.4
Fe	T	2.2443	2.2572	20.6123	− 500.7657	− 548.4277	− 47.6620	—
Mn	T	2.2320	2.2398	19.8164	− 501.5616	− 548.7212	− 47.1596	28.1

[a] T = tetrahedral conformation; SP = square planar conformation

[b] Binding energy of the 8-mercaptoquinoline anion = − 260.6890 (eV)

[c] Ref. [31]

Table 7. *A comparison between thermodynamic data* [11] *for chelation of transition metals with oxine and thio-oxine and the calculated enthalpies*

Element	Oxine (V)								Thio-oxine (VI)			
	ΔS_1	ΔS_2	ΔS^{tot}	ΔH_1	ΔH_2	ΔH^{tot}	$\log K^{tot}$	ΔE^{calc}	ΔS_1	ΔH_1	$\log K_1$	$\log K^{tot}$
Zn	23	28	51	− 5.9	− 3.7	− 9.6	18.15	− 15.7	26	− 7.2	11.0	25.7
Cu	27	26	53	− 10.2	− 9.4	− 19.6	25.90	− 21.8	9	− 14.7	12.7	32.4
Ni	17	11	28	− 9.3	− 10.0	− 19.3	20.27	− 16.4	12	− 11.4	11.0	25.2
Co	20	11	31	− 7.2	− 8.2	− 15.4	18.05	− 14.8	− 15	− 15.4	7.9	28.4
Mn	22	5	27	− 3.5	− 7.0	− 10.5	13.49	− 9.8	19	− 3.5	6.74	28.1

ΔS_1, ΔS_2 and ΔS^{tot} are the entropies of stepwise chelation for the mono-complex, bis-complex, and both respectively (eu) ΔH_1, ΔH_2 and ΔH^{tot} are the related enthalpies (kcal mol^{-1}). Log K_1 and log K^{tot} are the related stability constants. ΔE^{calc} is the calculated gas phase enthalpy (eV)

Calculations

All calculations were carried out on local IBM 3032 or 3083 Series computers using Program CINDO54 [1] which is dimensioned to accept up to 300 atoms and 500 basis functions and any element, in principle, up to Xenon. Crystallographic coordinates for the ligands and complexes described here were obtained directly from the Cambridge database [35] (mounted on a local VAX 11/750 computer). A modified molecular graphics package [36] was used for observing and modifying the transition metal templates and substituted derivatives. Data was generally submitted directly from a DEC VT11 screen display to the IBM mainframe for calculations.

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