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Formation Constants of Bivalent Metal Ion Complexes With Diphenyl Violuric Acid and Its Higher Analogues

Pavan Mathur[a], **D. P. Goel**[b], and **R. P. Singh**[a] *

[a] Department of Chemistry, University of Delhi, Delhi-110007, India
[b] St. Stephen's College, Delhi-110007, India

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Stability constants of transition-metal chelates of 1,3-disubstituted 5-hydroximino-hexahydropyrimidine-2,4,6-trione [diphenyl violuric acid (DPhVA) and di-*o*-, *m*-, and *p*-tolyl violuric acid (DiToVA)] have been determined in 75% dioxane (aqueous) at 30 ± 1 °C, in solutions containing an excess of the ligand at ionic strength $0.1 M$-$NaClO_4$. The order of formation constants found is:

$$UO_2 > Cu > Ni \geqslant Fe > Co > Pb > Zn > Cd > Mn.$$

The stability influencing effects of donor π-bond (metal to ligand) has been demonstrated. The effects of electrophilic and nucleophilic centres within the ligand have been correlated to stability constants and acid dissociation constants.

Komplexbildungskonstanten von bivalenten Metallen mit Diphenyl-violursäure und höheren Homologen

Die Stabilitätskonstanten von Übergangsmetallchelaten von 1,3-disubstituierten 5-Hydroximino-hexahydropyrimidin-2,4,6-trionen [Diphenyl-violursäure (DPhVA) und Di-*o*-, *m*- und *p*-tolyl-violursäure (DiToVA)] wurden in 75% wäßr. Dioxan bei 30 ± 1 °C unter Konstanthaltung der Ionenstärke ($0,1 M$-$NaClO_4$) bestimmt. Folgende Reihung wurde gefunden:

$$UO_2 > Cu > Ni \geqslant Fe > Co > Pb > Zn > Cd > Mn.$$

Der stabilitätsbeeinflussende Effekt von π-Donor-Bindungen (Metall—Ligand) wurde nachgewiesen. Effekte von elektrophilen und nucleophilen Zentren innerhalb der Liganden wurden mit Stabilitätskonstanten der Chelate und Dissoziationskonstanten der Säuren korreliert.

Complex equilibria studies of bivalent metal ions with diphenyl violuric acid (DPhVA) [5-hydroximino-1,3-diphenyl-hexahydropyrimidine-2,4,6-trione] and its higher analogues have

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received comparatively little attention. Some physical constants have been reported in the literature[1,2]. The present paper describes the pH-metric determination of acid dissociation constants of DPhVA and di-(-*o*, -*m*, -*p*)-tolyl derivatives of violuric acid (DiToVA); furthermore the formation constants of the corresponding complexes with some bivalent metal ions were determined.

Experimental Technique

A Beckman pH-meter, expandomatic SS-2 model, in conjunction with a glass and calomel electrode assembly, was used for pH measurements. The pH-meter was standardised with potassium hydrogen phthalate and phosphate buffers before performing the titrations.

Diphenyl violuric acid and di(-*o*, -*m*, -*p*)tolyl violuric acids were prepared by the general method outlined by *Dutt* and coworkers[3].

Solutions of these ligands were prepared in freshly distilled dioxane. All the metal ion solutions were prepared from the corresponding nitrates or sulphates and were standardised by conventional gravimetric procedures.

Chemically pure sodium perchlorate (Riedal) was used to keep the ionic strength constant. A $0.05M$ solution of tetramethyl ammonium hydroxide (TMAH) in 75% aqueous dioxane was used as titrant. The dioxane used was purified by refluxing over sodium wire for 24 h. and was freshly distilled over sodium before use. All other chemicals were of reagent grade.

All measurements were made at 30 ± 1 °C. Pre-saturated nitrogen (with 75% aqueous dioxan) was passed through the solutions during the titrations.

pH-Titration Procedure

The method of *Bjerrum* and *Calvin*, as modified by *Irving* and *Rossotti*[4], has been used to obtain the value of $\bar{n}$ and pL. The following solutions (total volume = 19.67 ml, due to contraction on mixing dioxane and water) were titrated potentiometrically against standard $0.05M$ TMAH solution to find $\bar{n}$ and pL values.

(i) 0.8 ml of $HClO_4$ ($0.02M$) + 1.0 ml of $NaClO_4$ ($2M$) + 2.7 ml of H_2O + 0.5 ml of $NaNO_3$ or Na_2SO_4 ($0.02M$) + 15.0 ml of dioxane.

(ii) 0.8 ml of $HClO_4$ ($0.02M$) + 1.0 ml of $NaClO_4$ ($2M$) + 2.7 ml of H_2O + 0.5 ml of $NaNO_3$ or Na_2SO_4 ($0.02M$) + 10.0 ml of ligand ($0.01M$) + 5.0 ml of dioxane.

(iii) 0.8 ml of $HClO_4$ ($0.02M$) + 1.0 ml of $NaClO_4$ ($2M$) + 2.7 ml of H_2O + 0.5 ml of metal nitrate or sulphate ($0.02M$) + 10.0 ml of ligand ($0.01M$) + 5.0 ml of dioxane.

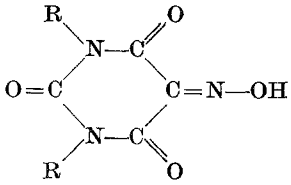
Calculations

The ligands exhibit keto-enol tautomerism and the proton of the —NOH group can be replaced by a metal ion in the hydroximino-ketonic form. However, in order to neutralize an alkali like TMAH, the original weakly acidic hydroximino-ketonic form has to tautomerize into the

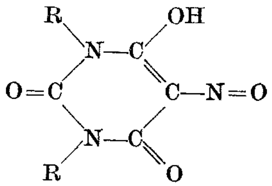
Table 1. *Stability constants of the metal complexes of diphenyl and tolyl derivatives of violuric acid and pK(OH) values for the ligands, at 0.1M*-$NaClO_4$

Ligand	DPhVA			Di-*p*-ToVA			Di-*m*-ToVA			Di-*o*-ToVA		
	$\log K_1$	$\log K_2$	$\log \beta_2$	$\log K_1$	$\log K_2$	$\log \beta_2$	$\log K_1$	$\log K_2$	$\log \beta_2$	$\log K_1$	$\log K_2$	$\log \beta_2$
H^+	7.48	—	—	5.56	—	—	6.08	—	—	6.38	—	—
Mn^{2+}	3.1000	2.8800	5.9800	2.2400	2.7100	4.9500	2.6000	2.7000	5.3000	2.7523	2.7043	5.4566
Cd^{2+}	4.3541	4.0356	8.3897	3.3820	2.1002	5.4822	—	—	6.0238	—	—	5.6825
Zn^{2+}	4.3000	4.4000	8.7000	3.8000	3.9523	7.7523	4.0422	3.6100	7.6522	4.2006	4.2498	8.4504
Pb^{2+}	4.2792	3.9732	8.2524	3.5434	4.3711	7.9145	3.7042	4.2678	8.0080	3.9523	4.1539	8.1062
Co^{2+}	5.3400	5.1900	10.5300	4.5800	4.2600	8.8400	4.6008	4.4400	9.0408	4.9402	4.3230	9.2632
Ni^{2+}	5.8880	5.5120	11.4000	4.9000	4.2752	9.1752	5.0302	4.7904	9.8206	5.4704	5.1898	10.6602
Fe^{2+}	5.8200	5.3700	11.1900	4.8900	4.0107	8.9007	4.8400	4.6100	9.4500	4.9308	4.7214	9.6522
Cu^{2+}	6.0600	5.7700	11.8300	5.1000	4.9885	10.0885	5.3502	5.0702	10.4204	5.8002	4.9004	10.7006
UO_2^{2+}	6.1767	5.9569	12.0336	5.3994	5.0236	10.4430	5.7001	5.3429	11.0430	6.0497	5.3120	11.3617

more acidic nitroso-enolic form[5]. The proton thus released by the nitroso-enolic form leaves a negative centre for complex formation.



(R = phenyl, tolyl)
Hydroximino-Ketonic Form



(R = phenyl, tolyl)
Nitroso-Enolic Form

From the titration curves of solutions (i) and (ii) the values of pK (OH) were calculated by plotting, $\log(\alpha/1 - \alpha)$ vs. pH (where α is the degree of dissociation); straight lines with an intercept equal to pK and a slope equal to unity were obtained. The pKa values are given in Table 1 along with the formation constants of various complexes.

From the titration curves of solutions (i), (ii), and (iii), $\bar{n}$ values of the metal complexes were determined at various pH values. From the knowledge of values of pK (OH) and those of $\bar{n}$ at different pH's, the corresponding values of pL have been calculated.

The stability constants were computed on an IBM360 computer using a weighted least squares program (in FORTRAN IV) patterned after that of *Sullivan et al.*[6]. The β_n values were initially approximated from the data ($\bar{n}$, pL) using weight factors of unity. Using these approximate β_n's the weight factors were calculated. Then an improved set of β_n's is obtained, and the iterative procedure was repeated till successive cycles gave a change < 0.00001 for each β_n.

The weighted least squares treatment determines that set of β_n's which makes the function U, $\left(U = \sum_{n=0}^{n} (y - x - nz)\, \beta_n x^n\right)$ nearest to zero, by minimizing S, $\left(S = \sum_{i=1}^{i} w_i U^2 \;(x_i,\; y_i,\; z_i)\right)$ with respect to variation in β_n (see lit.[6]).

We are reporting the $S_{\text{min.}}$ values for a series of metal complexes. $S_{\text{min.}}$ has the same statistical distribution as χ^2 with k degrees of freedom, and the weight defined in accordance with *Sullivan et al.*[6] we can put $S_{\text{min}} = \chi^2$ (Table 2).

$\bar{n}$ values greater than 2.0 have not been obtained in any of the cases. It is therefore concluded that not more than two complexes, i.e. 1:1, and 1:2 (M:L) are formed in each system.

In view of the very low ($5.0 \times 10^{-4} M$) concentration of metal ions used in the titrations, it has been assumed that the formation of polynuclear complexes is negligible.

Table 2. $S_{\min}$ *(*$S_{\min} = \chi^2$*) values for metal complexes of diphenyl and tolyl derivatives of violuric acid at 0.1M*-$NaClO_4$

Ligand	DPhVA $S_{\min}$	Di-*p*-ToVA $S_{\min}$	Di-*m*-ToVA $S_{\min}$	Di-*o*-ToVA $S_{\min}$
Mn^{2+}	0.10021	0.20011	0.10807	0.08079
Cd^{2+}	0.63081	0.32561	0.22024	0.12396
Zn^{2+}	0.25096	0.27024	0.19525	0.30293
Pb^{2+}	0.20487	0.86706	0.23602	0.41123
Co^{2+}	0.51182	0.19241	0.088390	0.51182
Ni^{2+}	0.09886	0.64240	0.22031	0.20599
Fe^{2+}	0.14803	0.43223	0.19807	0.21127
Cu^{2+}	0.16490	0.24325	0.20712	0.73956
UO_2^{2+}	0.13908	0.097571	0.098762	0.26049

Results and Discussion

I. Effect of the Carbonyl Group

The experimental results reveal that *pKa* values for diphenyl- resp. ditolyl-violuric acid are higher than the *pKa* values of the corresponding acids in the series of substituted thio violuric acids[8].

This is likely because the carbonyl group between the two nitrogen atoms tends to withdraw electrons from the centre of chelation thus making the process of tautomerisation of the ligand to the nitroso-enolic form somewhat difficult; in other words it stabilizes the hydroximino-ketonic form.

The ionization of the proton depends upon the ease of conversion into the nitroso-enolic form. Thus a hindered tautomerization leads to ionization of the proton at higher pH values. Hence the *pKa* values will be higher.

II. Stability Constants and Proton Dissociation Constants

Table 1 shows that the *pKa* and equilibrium constants of the metal-ligand complexes follow the decreasing order.

$$\text{DPhVA} > \text{Di-}o\text{-ToVA} > \text{Di-}m\text{-ToVA} \geqslant \text{Di-p-ToVA}$$

The methyl group by virtue of its inductive effect enhances the electron density in the phenyl ring; thus the tolyl group will act as a nucleophilic substituent and opposes the electrophilic effect of the carbonyl ($\geqslant C=O$) group.

Due to this effect the ditolyl derivatives have lower *pKa* values compared to the diphenyl derivative of violuric acid. The nucleophilic power of the tolyl group follows the decreasing order[9]:

$$p\text{-tolyl} \geqslant m\text{-tolyl} > o\text{-tolyl}.$$

The *pKa* values, therefore, follow the reverse order.

III. Stabilization Effect of the π-Donor Bond

Considering a possible metal ligand donor π-bond in these complexes[10, 11] which is favored by an electrophilic substituent (stabilization of the π-acceptor capability of the ligand[12]), the values of log K_1 log K_2 and log β_2 have been plotted against atomic number of central metal atoms. The differences between the Mn-Zn line and the other complexes are shown in Table 3. These data reveal that the general order of increased stabilization is:

$$\text{Di-}p\text{-ToVA} \leqslant \text{Di-}m\text{-ToVA} < \text{Di-}o\text{-ToVA} < \text{DPhVA}$$

Table 3. *Ligand field stabilization*

Metal	Ligands	ΔK_1	ΔK_2	$\Delta \beta_2$
	DPhVA	2.50	2.17	4.70
Fe^{2+}	*o*-ToVA	1.87	1.80	3.60
	m-ToVA	1.96	1.75	3.70
	p-ToVA	2.20	1.10	3.40
	DPhVA	1.78	1.70	3.50
Co^{2+}	*o*-ToVA	1.64	1.10	2.60
	m-ToVA	1.44	1.40	2.80
	p-ToVA	1.68	1.10	2.74
	DPhVA	2.08	1.70	3.80
Ni^{2+}	*o*-ToVA	1.85	1.65	3.41
	m-ToVA	1.57	1.60	3.07
	p-ToVA	1.70	0.90	2.57
	DPhVA	2.02	1.67	3.65
Cu^{2+}	*o*-ToVA	1.90	1.00	2.85
	m-ToVA	1.59	1.55	3.22
	p-ToVA	1.66	1.30	2.75

References

[1] *R. P. Singh*, Curr. Sci. **24**, 208 (1955).
[2] *R. P. Singh*, Ph.D. Thesis, University of Delhi, 1960.
[3] *S. Prakash* and *S. Dutt*, Proc. Natl. Acad. Sci. (India) **29** (1938).
[4] *H. M. Irving* and *H. S. Rossotti*, J. Chem. Soc. **1953**, 3397.
[5] *S. Prakash* and *S. Dutt*, Proc. Natl. Acad. Sci. (India) **29** (1938).
[6] *J. C. Sullivan*, *J. Rydberg*, and *W. F. Miller*, Acta. Chem. Scand. **13**, 2023 (1959).
[7] *J. Rydberg* and *J. C. Sullivan*, Acta Chem. Scand. **13**, 2059 (1959).
[8] *Pavan Mathur*, *D. P. Goel*, and *R. P. Singh*, Ind. J. Chem., in press.
[9] *I. L. Finar*, Organic Chemistry, Vol. 1. The English Language Book Soc. and Longmans, Green and Co., Ltd. 1967.
[10] *K. Burger* and *I. Ruff*, *Talanta* **10**, 329 (1963).
[11] *B. A. Jillot* and *R. J. P. Williams*, J. Chem. Soc. **1958**, 462.
[12] *K. Burger* and *I. Egyed*, J. Inorg. and Nucl. Chem. **27**, 2631 (1965).