Reactions of Metal Ions with Triketones in Solution. Part 1. Formation Constants for the Systems of Heptane-2,4,6-trione, 1-Phenylhexane-1,3,5-trione, 1,5-Diphenylpentane-1,3,5-trione, and 2,2′-Dihydroxybenzophenone with Proton, Nickel(II), and Cobalt(II)

Michael J. Hynes * **and James Walsh**
Chemistry Department, University College, Galway, Ireland

The equilibrium constants for the proton reactions of heptane-2,4,6-trione, 1-phenylhexane-1,3,5-trione, 1,5-diphenylpentane-1,3,5-trione, and 2,2′-dihydroxybenzophenone have been determined in methanol–water solutions (70:30 v/v) using potentiometric and spectrophotometric methods. The compositions and log β values of the complexes formed in solution by these ligands with nickel(II) and cobalt(II) have also been determined. All four ligands form 1:1 and 2:2 complexes with these metal ions.

β,δ-Triketone analogues of β-diketones exist in solution as equilibrium mixtures of triketo, mono-enol, and bis-enol forms. The ligands behave as dibasic acids (H_2L) and they form metal complexes in which they may be either bidentate or tridentate.[1,2] A considerable number of metal complexes with these ligands have been prepared and the structures of a number have been determined by *X*-ray crystallography. The π-system of the dianion, with the consequent preference for a planar configuration apparently precludes tridentate co-ordination by these ligands to a single metal atom. Instead, binuclear 2:2 complexes are formed in which the central oxygen of the triketone is bonded to two metal atoms.

To date most of the investigations of metal complexes of triketones have been concerned with the solid-state structures and magnetic properties of these compounds. Little investigation of the stoicheiometric compositions and stabilities of the species present in solution has been carried out. As part of our continuing interest in the reactions of metal ions with β-diketones and related species we have investigated the reactions of a number of these ligands with various metal ions in solution. We now report the stability constants for reaction of nickel(II) and cobalt(II) with heptane-2,4,6-trione (H_2hto), 1-phenylhexane-1,3,5-trione (H_2phto), 1,5-diphenylpentane-1,3,5-trione (H_2dppta), and 2,2′-dihydroxybenzophenone (H_2dhbpo).

Experimental

Heptane-2,4,6-trione was prepared according to the method of Bethell and Maitland[3] and was purified by distillation under reduced pressure. Freshly distilled material was used for the titrations. 1-Phenylhexane-1,3,5-trione and 1,5-diphenylpentane-1,3,5-trione were prepared according to Hauser and Harris.[4] 2,2′-Dihydroxybenzophenone was prepared as previously described.[5] Solutions of the ligands were standardized by titration with standard sodium hydroxide. Endpoints were determined using an iterative computer program based on the method of Gran and Johansson.[6] Stock solutions of Ni^{II} and Co^{II} were prepared from the nitrates (BDH). These solutions were standardized by titration with ethylenediaminetetraacetate. Methanol was purified by distillation from magnesium and iodine. All solutions were prepared using distilled water which had been boiled for 15 min. Methanol–water solutions (70:30 v/v) were prepared by adding water (300 g) to a volumetric flask (1 000 cm^3) and diluting to the mark with dry methanol. The mole fraction of methanol in these solutions is 0.508.[7] Sodium perchlorate purified as previously described[8] was used to adjust the ionic strength of all solutions to 0.5 mol dm^{-3}.

Values of pH were measured using a Pye model 290 pH meter equipped with a Pye Ingold $E_7{}^0$ combination electrode. The potassium chloride solution in the electrode compartment was replaced by 3 mol dm^{-3} sodium chloride solution. The pH readings were converted to hydrogen ion concentration as described by Agrawal.[7]

Titrations were carried out in purpose-built jacketed beakers through which water at 25.0 ± 0.1 °C was circulating. All titrations were carried out under an atmosphere of nitrogen gas which had been bubbled through an aqueous solution having the same ionic strength as the solution being titrated.

In the case of H_2hto the second p*K* was too high to be reliably determined using the potentiometric method, and it was therefore determined spectroscopically. The spectra of seven solutions of H_2hto (2.5×10^{-5} mol dm^{-3}) containing various concentrations of sodium hydroxide were recorded in the wavelength range 280—380 nm using a Cary 118 spectrophotometer. The absorbances at 5-nm intervals were digitized and were used as the input data for the SQUAD program.[9]

In the case of potentiometric data, stability constant refinement was carried out using MINIQUAD-75[10,11] and SCOGS,[12] and the deviations quoted are those given by the programs. In all cases various models were tried and the final model was selected on the basis of the sum of the squared residuals and the MINIQUAD crystallographic *R*-factor.

In the case of the complexes of Ni^{2+} with H_2dhbpo and H_2phto the proposed models were extensively tested by carrying out titrations over a six-fold range of ligand to metal concentration. The metal concentration used was 1.0×10^{-3} mol dm^{-3} and the ligand concentration was varied in the range 5×10^{-4} to 3×10^{-3} mol dm^{-3}. In all, four titrations were carried out on each system and it was found that the stability constants did not change appreciably with change in the ligand to metal ratio.

If plots of $\bar{Z}$ (the degree of formation) against pL (L = free ligand concentration) are recorded for different total ligand and metal concentrations, in the absence of hydroxo, protonated, and polynuclear species the plots should overlap. When these conditions are not valid the $\bar{Z}$ and pL functions are really pseudo-$\bar{Z}$ and -pL and the plots of $\bar{Z}$ against pL will diverge. Thus these plots can be used to show how well a particular set of constants describes the experimental data. The proposed set of constants together with the experimental data (concentrations, volumes, pH's) was used as input for SCOGS and an output of

Table. Log β_{pqr} for the species $L_pM_qH_r$ at 25 °C and $I = 0.5$ mol dm^{-3} (Na[ClO$_4$]) in methanol–water (70:30 v/v) (s = standard deviation in log constants)

H_2L	M	p	q	r	log β	s	Program
H_2hto							
		1	0	1	12.39	0.05	SQUAD
		1	0	2	20.66	0.05	MINIQUAD
	Ni^{II}	1	1	1	18.99	0.01	MINIQUAD + SCOGS
	Ni^{II}	2	2	0	24.66	0.03	MINIQUAD
	Ni^{II}	2	2	0	24.62	0.03	SCOGS
	Co^{II}	1	1	1	18.46	0.01	MINIQUAD
	Co^{II}	1	1	1	18.45	0.01	SCOGS
	Co^{II}	2	2	0	22.97	0.03	MINIQUAD
	Co^{II}	2	2	0	22.91	0.04	SCOGS
H_2phto							
		1	0	1	11.08	0.02	MINIQUAD
		1	0	2	19.47	0.02	MINIQUAD
	Ni^{II}	1	1	1	16.89	0.03	MINIQUAD
	Ni^{II}	1	1	1	16.90	0.04	SCOGS
	Ni^{II}	2	2	0	19.94	0.08	MINIQUAD
	Ni^{II}	2	2	0	19.93	0.06	SCOGS
	Co^{II}	1	1	1	16.35	0.02	MINIQUAD + SCOGS
	Co^{II}	2	2	0	18.14	0.06	MINIQUAD
	Co^{II}	2	2	0	18.13	0.06	SCOGS
H_2dppta							
		1	0	1	10.74	0.02	MINIQUAD
		1	0	2	19.01	0.02	MINIQUAD
	Ni^{II}	1	1	1	16.97	0.03	MINIQUAD + SCOGS
	Ni^{II}	2	2	0	23.31[a]	0.52	MINIQUAD
	Ni^{II}	2	2	0	24.36[a]	0.51	SCOGS
	Co^{II}	1	1	1	16.29	0.01	MINIQUAD
	Co^{II}	2	2	0	*b*		
H_2dhbpo							
		1	0	1	10.38	0.01	MINIQUAD
		1	0	2	19.95	0.01	MINIQUAD
	Ni^{II}	1	1	1	14.97	0.01	MINIQUAD
	Ni^{II}	1	1	1	14.96	0.01	SCOGS
	Ni^{II}	2	2	0	16.32	0.01	MINIQUAD + SCOGS
	Co^{II}	1	1	1	14.41	0.05	MINIQUAD + SCOGS
	Co^{II}	2	2	0	15.88	0.03	MINIQUAD + SCOGS

[a] Only approximately 10% of the 2:2 complex was formed before the onset of precipitation. [b] Precipitate formed before appreciable formation of 2:2 complex.

pH against simulated (theoretical) titrant (cm^3) was obtained. These data were then used to produce theoretical plots of $\bar{Z}$ against pL for different titrations. These may then be compared with the experimental data which are superimposed on the plots in the form of experimental points using different symbols for the different titrations. A computer program was written to carry out the calculations and draw the plots. Proton n.m.r. measurements were recorded using a JEOL MH 100 spectrometer.

Results and Discussion

The reaction between the triketones, metal ion, and proton is conveniently represented by equation (1) (charges omitted), the

$$pL + qM + rH \longrightarrow L_pM_qH_r \qquad (1)$$

formation constant for this generalized reaction being β_{pqr}. The Table shows the formation constants determined in this study. Where there is a disparity between the values calculated using MINIQUAD and SCOGS both β values are given. However, in most instances the disparity is quite small.

The first pK values (pK_1) of H_2hto, H_2phto, and H_2dppta are approximately the same. The second pK of H_2hto is considerably higher than that of the other three ligands. The pK_1 of H_2dhbpo is much higher than any of the other ligands while pK_2 is only one unit higher. This illustrates the relative independence of the two benzene rings in this ligand.

All four ligands form 1:1 and 2:2 complexes with both Ni^{II} and Co^{II}. The 1:1 complexes are formed at low pH while at higher pH values they are converted to the 2:2 complexes. Figure 1 shows the distribution of the 1:1 and 2:2 complexes of Ni^{II} as a function of pH for all four ligands. The concentrations of the various species in solution were calculated using COMICS.[13]

As described in the Experimental section, the reactions of Ni^{II} with H_2dhbpo and H_2phto to form the 1:1 complexes were extensively investigated. Figures 2 and 3 show the plots of $\bar{Z}$ against pL for these ligands and it is readily apparent that the constants in the Table which were used to produce these plots are an adequate description of the systems. The solid line

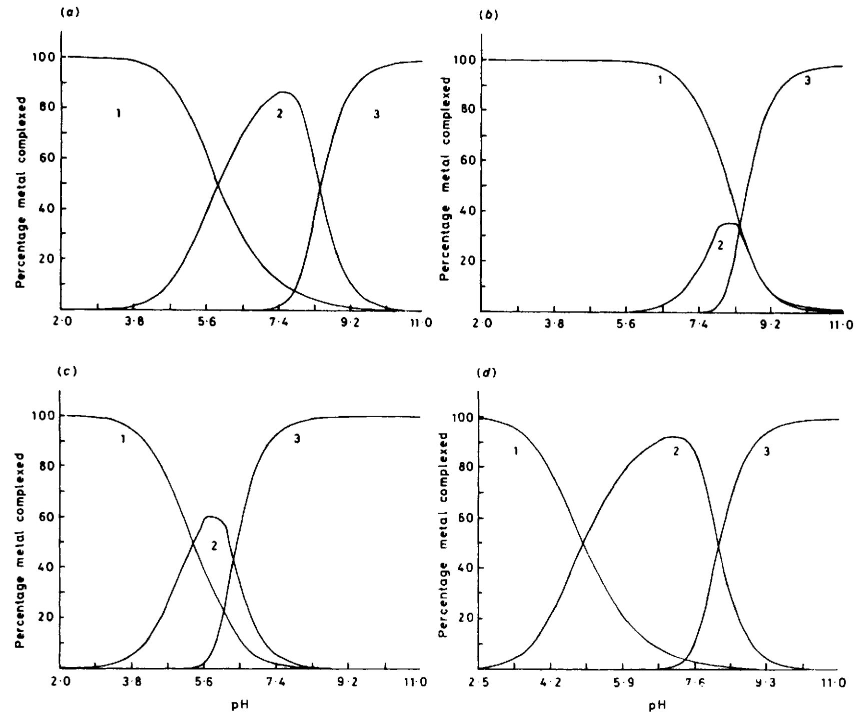

Figure 1. COMICS[13] computed distribution of free metal and complex species with pH for the nickel(II) complexes of (*a*) H_2phto, (*b*) H_2dhbpo, (*c*) H_2dppta, and (*d*) H_2hto. In each case the total metal and ligand concentrations are 1×10^{-3} mol dm^{-3}: (1) free metal, (2) 1:1 complex, (3) 2:2 complex

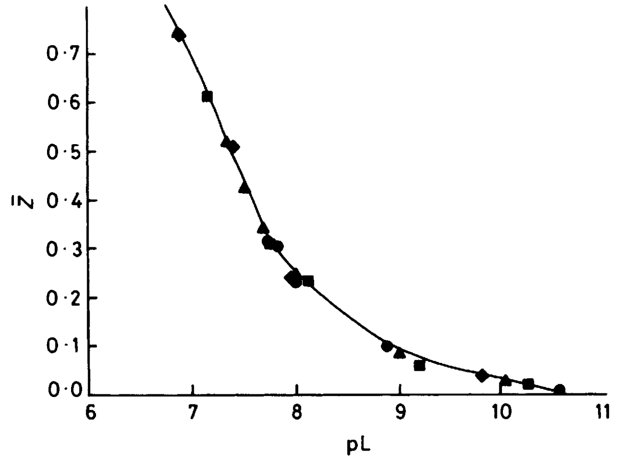

Figure 2. Plot of $\bar{Z}$ against pL for reaction of Ni^{2+} with H_2dhpbo in methanol–water (70:30 v/v) at 25 °C and $I = 0.5$ mol dm^{-3}: [H_2dhbpo] = 5×10^{-4} (●), 1×10^{-3} (▲), 2×10^{-3} (◆), and 3×10^{-3} mol dm^{-3} (■); [Ni^{2+}] = 1×10^{-3} mol dm^{-3}

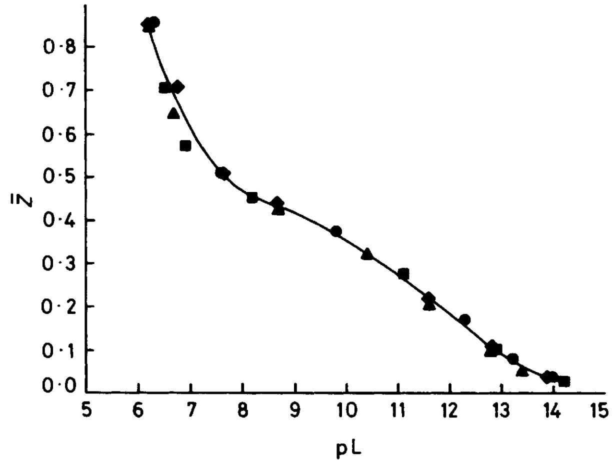

Figure 3. Plot of $\bar{Z}$ against pL for reaction of Ni^{2+} with H_2phto in methanol–water (70:30 v/v) at 25 °C and $I = 0.5$ mol dm^{-3}; [H_2phto] = 5×10^{-4} (●), 1×10^{-3} (▲), 2×10^{-3} (◆), and 3×10^{-3} mol dm^{-3} (■); [Ni^{2+}] = 1×10^{-3} mol dm^{-3}

represents the best curve through the theoretical data at various ligand to metal ratios. The experimental points for the various titrations clearly lie on this curve. (Only a selection of the experimental points are actually shown).

For the 1:1 stability constants of Ni^{II} the relative stability order is in the ratio H_2hto:H_2dppta:H_2phto:H_2dhbpo, 102:44:17:1; for Co^{II} the order is in the ratio H_2hto:H_2dppta:H_2phto:H_2dhbpo, 110:33:17:1. The ratios were derived from the values of K_{MHL} where $K_{MHL} = \beta_{111}/\beta_{101}$. For the 2:2 complexes the order of relative ratios of the stability constants is in the sequence H_2hto:H_2dppta:H_2phto:H_2dhbpo, $10^{8.3}$:$10^{8.04}$:$10^{3.61}$:1 for Ni^{II}, and $10^{7.03}$: – :$10^{2.25}$:1 for Co^{II}. In all cases the Ni^{II} complexes are more stable than the Co^{II} complexes.

The low stability of the complexes with H_2dhbpo is readily explained in terms of 'crossed resonance' effects.[14] The double bond between the two carbons attached to the enolate oxygen is also part of the resonating aromatic ring. Using the notation of Pauling[15] and Branch and Calvin[16] the double bond adjacent to the enolate oxygen is assigned a bond order of 1.5, compared to 2 in pentane-2,4-dione. This greatly reduces the effectiveness of the enolate resonance and consequently the stability of the metal chelate. It has also been suggested that the hydrogen atoms in the 6 and 6′ positions of the free ligand interfere with each other sterically[17] and this may cause some distortion around the metal atom.

It has been shown that in the case of β-diketones there is a linear relationship between the pK of the ligand and[18] the log of the formation constant. However, this relationship is not universal and only applies when the end groups are similar, and indeed β-diketones with different end groups give different lines. In general, β-diketones containing methyl end groups form less stable complexes than β-diketones having two ring systems as end groups. However the 1:1 complexes of H_2dppta are less stable than those of H_2hto (allowing for the effect of pK_2 on β_{MHL}). The reduced stability of the complex with mixed end groups is not immediately understandable, for example in water–dioxane the stabilities of benzoylacetone complexes are somewhat higher than those of pentane-2,4-dione.

Proton n.m.r. measurements of solutions of H_2phto in $CDCl_3$ and Me_2SO containing increasing amounts of Mg^{2+} show increasing shifts of the benzene protons, while the terminal CH_3– protons remain unshifted. This strongly suggests that complexing involves the two oxygen atoms adjacent to the benzene ring.

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