

THERMOCHROMISM OF METAL CHELATES WITH TRIPHENYLMETHANE COMPLEXONS
IN AQUEOUS SOLUTIONS

Shoji NAKADA, Mutsuo YAMADA, Tasuku ITO, and Masatoshi FUJIMOTO
Department of Chemistry, Faculty of Science, Hokkaido University, Sapporo 060

Reversible thermochromisms are found for about thirty kinds of metal complexes of triphenylmethane complexons in aqueous solutions. The color changes are primarily due to the equilibria between the complex having an uncoordinated phenolic hydroxyl group and the complex having a coordinated phenolate group.

In the present study we found that the metal chelates of triphenylmethane complexons* are thermochromic in aqueous media.

Figure 1 shows the structures and the abbreviated nomenclatures of the ligands. Complexes of Mg^{2+} , Ca^{2+} , Mn^{2+} , Co^{2+} , Ni^{2+} , Cu^{2+} , and Zn^{2+} were studied. Color changes of the aqueous solutions containing triphenylmethane complexons and 10-100 fold excess of metal ions have been studied at various buffered pH as a function of temperature by measurements of visible absorption spectra as well as by visual observation of color changes. The color changes occurred in the narrow pH range which is characteristic for each system. Some of the results are summarized in Table 1. The metal complexes containing the ligands, in which two benzene rings are bonded through an ether linkage as shown in Fig. 2, were not thermochromic.

As a typical example, the visible absorption spectra of the Cu(II)-XO system at various temperatures are shown in Fig. 3. The solution containing XO and $Cu(ClO_4)_2$ in excess remarkably exhibits thermochromism at pH 3.5-5.0. The solution is orange at the lower temperature and reddish violet at the higher temperature in the range from 2 to 90 °C. As the temperature rises, the absorption at 450 nm decreases with an increase in the absorption at 574 nm. The absorption spectra at various temperatures have a well-defined isosbestic point at 490 nm, and the temperature-dependence of the spectrum was fully reversible. The absorption at the longer wavelength is associated with the 2 : 1 Cu(II)-XO complex having a coordinated phenolate group.¹⁾ The composition of Cu(II)-XO complex responsible for the absorption at the longer wavelength was determined at various temperatures by the molar-ratio method. The metal to ligand ratio was found to be 2 : 1 at any temperature.²⁾ On the other hand, the absorption maximum at the shorter wavelength ($\lambda_{max} = 450$ nm) is different from that of the free ligand in this pH region ($\lambda_{max} = 434$ nm). The absorbing species is the Cu(II)-complex coordinated only by the iminodiacetic acid groups but not by the phenolic hydroxyl group.³⁾

* Triphenylmethane complexons denote a series of multidentate ligands derived from the triphenylmethane dyes and iminodiacetic acid or other amino acids.

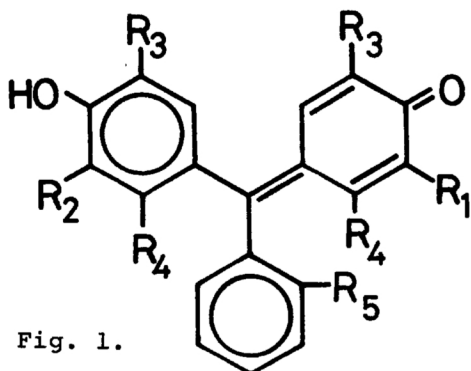


Fig. 1.

Ligand ^{a)}	R ₁ ^{b)}	R ₂ ^{b)}	R ₃	R ₄	R ₅
XO	A	A	CH ₃	H	SO ₃ H
MXB	A	A	CH ₃	CH ₃	SO ₃ H
MTB	A	A	CH(CH ₃) ₂	CH ₃	SO ₃ H
CO	A	A	H	H	SO ₃ H
GCR	B	B	CH ₃	H	SO ₃ H
SCR	C	C	CH ₃	H	SO ₃ H
SXO	A	H	CH ₃	H	SO ₃ H
PC	A	A	CH ₃	H	COOH
PPC	A	A	H	H	COOH
TPC	A	A	CH(CH ₃) ₂	CH ₃	COOH

a) XO: Xylenol Orange, MXB: Methylxylenol Blue, MTB: Methylthymol Blue, CO: Cresol Orange,⁴⁾ GCR: Glycine Cresol Red, SCR: Sarcosine Cresol Red; SXO: Semi-Xylenol Orange; PC: Phthalein Complexon, PPC: Phenolphthalein Complexon, and TPC: Thymolphthalein Complexon. b) A = CH₂N(CH₂COOH)₂, B = CH₂NHCH₂COOH, C = CH₂N(CH₃)CH₂COOH.

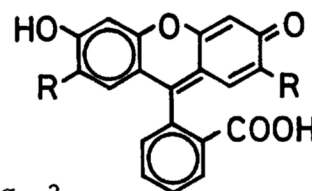
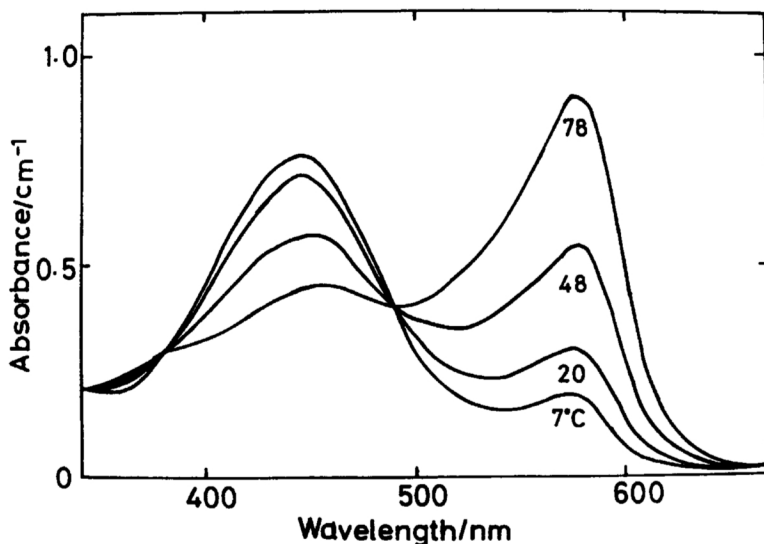


Fig. 2.

Calcein (R = CH₂N(CH₂COOH)₂) and Methyl Calcein (R = CH₂N(CH₃)CH₂COOH).

Fig. 3. Absorption spectra of the solution containing 1.2 x 10⁻⁴ mol dm⁻³ Cu²⁺ and 3.0 x 10⁻⁵ mol dm⁻³ XO at pH 3.94 and I = 0.1 mol dm⁻³ at various temperatures.

The temperature-dependence of the spectrum was quite similar to the pH-dependence of the spectrum. The effect of heating the system was essentially the same as the effect of an increase in pH of the solution, judging from the spectral changes. The positions of the absorption maxima and the isosbestic points are almost identical with each other for both spectral changes. It was confirmed that the temperature-dependence of the pH of acetate buffer solution is very small, e.g., pH 4.55 at 20 °C and pH 4.72 at 90 °C.

These facts indicate clearly that the observed thermochromism is primarily due to the equilibria between the complex AH having an uncoordinated phenolic hydroxyl group and the complex A having a coordinated phenolate group,



The complex A is predominant at the higher temperature.

The proposed mechanism suggests that pH decreases with an increase in temperature when the experiments are carried out in unbuffered solutions. When the pH of

Table 1. Thermochromisms of Some Metal Chelates with Triphenylmethane Complexons.^{a)}

No.	Ligand	Metal ion	pH ^{b)} at 25 °C	Color ($\lambda_{\max}/\text{nm}^{\text{c)}$)		Remark ^{d)}
				at room temperature	at 60 °C	
1	XO	Co ²⁺	3.99	orange (452)	reddish violet (584)	s
2		Ni ²⁺	3.64	orange (452)	reddish violet (584)	s
3		Cu ²⁺	4.21	orange (450)	reddish violet (574)	vs
4		Zn ²⁺	3.97	orange (448)	reddish violet (572)	vs
5	MXB	Mg ²⁺	6.72	pale blue (450)	blue (606)	s
6		Mn ²⁺	5.04	yellow (446)	blue (615)	vs
7		Co ²⁺	3.81	pale yellow (468)	blue (618)	s
8		Ni ²⁺	3.80	yellow (456)	blue (618)	s
9		Cu ²⁺	4.34	yellow (460)	dark blue (600)	s
10		Zn ²⁺	4.06	dark yellow (464)	blue (610)	vs
11	MTB	Mg ²⁺	5.75	yellow (438)	yellow green (600)	s
12		Ca ²⁺	5.85	yellow green (438)	green (600)	s
13		Mn ²⁺	5.85	yellow (438)	green (605)	vs
14		Co ²⁺	3.67	yellow (460)	dark green (615)	vs
15		Ni ²⁺	3.67	yellow (446)	yellow green (618)	vs
16		Cu ²⁺	5.19	brown (444)	brown violet (600)	s
17		Zn ²⁺	3.80	yellow (454)	dark blue (598)	vs
18	CO	Cu ²⁺	4.38	orange (460)	pink (563)	s
19	GCR	Co ²⁺	5.24	dark yellow (438)	reddish violet (579)	s
20		Cu ²⁺	3.46	dark yellow (440)	reddish violet (576)	s
21	SCR	Co ²⁺	4.45	yellow (434)	reddish violet (578)	vs
22		Ni ²⁺	4.47	yellow (438)	reddish violet (578)	vs
23		Cu ²⁺	3.50	pale yellow (444)	reddish violet (572)	s
24		Zn ²⁺	4.82	yellow (444)	reddish violet (570)	vs
25	SXO	Cu ²⁺	5.46	orange (464)	reddish violet (570)	s
26	PC	Mg ²⁺	6.42	colorless (—)	violet (574)	vs
27		Mn ²⁺	5.27	pale violet (—)	violet (578)	vs
28		Ni ²⁺	4.82	colorless (—)	violet (580)	vs
29	PPC	Mg ²⁺	6.90	pale pink (—)	reddish violet (556)	vs
30	TPC	Mg ²⁺	7.11	colorless (—)	pale blue (608)	vs
31		Mn ²⁺	6.41	colorless (—)	blue (614)	s
32		Ni ²⁺	5.15	pale blue (—)	blue (618)	vs

a) Observed for the solutions containing $(1-5) \times 10^{-5}$ mol dm⁻³ ligand and 10-100 fold excess of metal perchlorate. b) The pH, at which the remarkable thermochromic change was observed. Acetate buffer (CH₃COOH-CH₃COONa) and phosphate buffer (NaH₂PO₄-Na₂HPO₄) were used for the pH adjustment. c) λ_{\max} 's represent the positions of the absorption maxima of the shorter- or the longer-wavelength absorptions. — denotes no, weak, or broad absorption. d) s: strong, vs: very strong.

the solution containing 1.6×10^{-2} mol dm⁻³ Cu(ClO₄)₂ and 4.0×10^{-3} mol dm⁻³ XO (I = 0.1 mol dm⁻³ (NaClO₄)) was adjusted only with HClO₄ and NaOH, the pH decreased as expected from 4.5 to 4.0 for a temperature-rise from 25 to 90 °C with the same color change as in the case of the buffered solution. Furthermore, the thermochromic effect depends strongly on the pH of the solution and increases the most around pH 4.5 (Fig. 4), which corresponds to the pK value for the eq. 1 (4.55 at 25 °C³⁾). This fact also supports the proposed mechanism.

The systems No. 1-25 in Table 1 contain the complexes of sulfonphthalein complexons. The absorption spectra of these complexes in visible region consist of two absorption bands as the spectrum of the Cu(II)-XO system does (see Fig. 3). Temperature-dependencies of the spectra of these complexes were similar to that

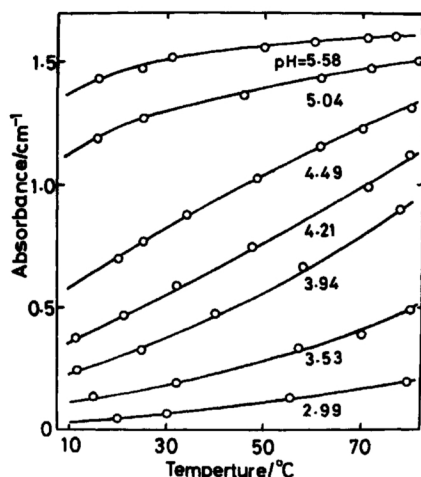


Fig. 4. Temperature dependence of the absorbance at 574 nm at various pH. The concentrations of Cu^{2+} and XO and the ionic strength I are the same as in Fig. 3.

shown in Fig. 3, i.e., with a temperature-rise, the absorptions at longer wavelength increase, whereas those at the shorter wavelength decrease. On the other hand, the absorption spectra of the systems No. 26-32, which contain the complexes of phthalein complexons, have only one band in visible region in the pH range where thermochromic effects are observed. The absorptions at 550-620 nm increase in intensities with a temperature-rise. Judging from the positions of the absorption bands, the complexes responsible for the absorptions have a coordinated phenolate group.

On these bases, it is concluded that the thermochromisms observed in the present study are primarily due to the equilibria between the complex having an uncoordinated phenolic hydroxyl group and the complex having a coordinated phenolate group.

In addition, molar absorptivities were found to depend on temperature for the XO complex of Cu^{2+} and also for the free ligand XO. Therefore, temperature-dependencies of the molar absorptivity might also take part in the thermochromic behaviors of the present complexes, though the effect is not so strong.

Free ligand also showed thermochromic behavior in neutral or weakly basic media, though the thermochromic effects of free ligands are much weaker than those of their metal complexes. The absorbance of the free ligand XO at 580 nm produced 19% increase in intensity at pH 6.40 for temperature-rise from 15 to 35 °C, while that of the Cu(II)-XO system at 574 nm did 36% at pH 4.50 for the same temperature-rise. Thermochromisms of the free ligands are primarily due to the protonation and the deprotonation of the phenolic hydroxyl group.

Temperature-jump studies were carried out preliminarily for the Co(II)-XO , Ni(II)-XO , Cu(II)-XO , and Zn(II)-XO systems in the pH range where the thermochromisms are observed. Though the feature of the spectral change due to the temperature change of these complexes are quite similar to each other, their relaxation times are different from each other and were found to be in the range of 50-100 ms, 2-5 μs , 2-5 μs , and 5-10 ms for the XO complexes of Co^{2+} , Ni^{2+} , Cu^{2+} , and Zn^{2+} , respectively. The quantitative studies by the temperature-jump method are now in progress and will be reported elsewhere.

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