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Thermochromism of Metal Chelates with Triphenylmethane Complexons in Aqueous Solutions. IV. Carbon-13 Nuclear Magnetic Resonance Studies of Xylenol Orange (XO) and Its Zinc(II) Complex†

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Reversible thermochromism of a Zn(II) complex with 3,3′-bis[bis(carboxymethyl)aminomethyl]-*o*-cresolsulfonphthalein (Xylenol Orange, XO) was studied in D_2O by means of the ^{13}C NMR method with reference to the data of spectrophotometric and temperature-jump measurements. ^{13}C NMR spectra of XO were measured in the pD range between 2.0 and 11.0 and the signals were assigned. π-Electron conjugations in XO and Zn(II)–XO spread on phenol- and quinonoid-rings through the central carbon atom, but the phenyl ring having an SO_3^- substituent is not involved in the π-conjugated system. The temperature- and the pD-dependences of ^{13}C NMR spectra of the Zn(II)–XO complex show that the thermochromism is caused by the temperature-dependence of a protolytic equilibrium of a phenolic hydroxyl group of the Zn(II)–XO complex.

In previous papers, thermochromisms observed for the Cu(II) complexes with triphenylmethane complexons (TPMC), Xylenol Orange (XO),[1] Methylthymol Blue (MTB),[2] and Methylxylenol Blue (MXB),[2] were interpreted in terms of the temperature-dependence of a protolytic equilibrium between a complex species AH having an uncoordinated free phenolic hydroxyl group and a complex species A having a coordinated phenolate group:

$$\mathrm{AH} \rightleftharpoons \mathrm{A} + \mathrm{H}. \qquad (1)$$

In the present paper, we aimed at studying thermochromism of metal chelates with TPMC by the ^{13}C NMR method. We chose a diamagnetic Zn(II) complex of XO, which is remarkably thermochromic.[1] The ^1H NMR spectrum of XO[3,4] is too complicated for the present purpose. Since the ^{13}C NMR spectrum of XO has not been reported, the related compounds were also examined for ^{13}C signal assignments of XO.

Experimental

Materials. XO was synthesized by Mannich condensation from *o*-Cresol Red (*o*-CR), iminodiacetic acid (IDA), and formaldehyde.[5] A crude sample of the synthesized XO purified beforehand through a cellulose column was finally purified by means of high-performance liquid chromatography (HPLC).[6] The purified XO was used as a free acid form. Anhydrous zinc(II) chloride[7] was used for the NMR measurements. Zinc(II) perchlorate was used for equilibrium and kinetic measurements. Reagent grade Aurin, Phenol Red (PR), *o*-CR, and IDA were used. The purity of these triphenylmethane derivatives was checked by analytical HPLC with a column of Microbondapak C_{18} (4 × 300 mm) and water–methanol (50/50, v/v) as a solvent. Deuterium oxide (99.7%), *ca.* 37% DCl in D_2O, and *ca.* 40% NaOD in D_2O were purchased from E. Merck, Ltd.

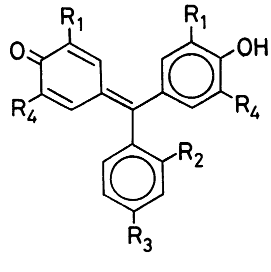
Measurements. The carbon-13 Fourier transform NMR spectra were measured in D_2O solutions at 25.0 MHz with a JEOL JNM-FX-100/PFT-100 spectrometer at various temperatures. The sample was held in a 5 mm tube. The sample concentration was adjusted to 200 mg cm^{-3} for $ZnCl_2$, 100 mg cm^{-3} for IDA and XO, and 40 mg cm^{-3} for Aurin, *o*-CR, and PR. Dioxane was used as an internal reference. Chemical shifts are expressed by δ as δ(dioxane) = 67.4.[8] The spectral width was 5000 Hz covered by 4096 addresses in the Fourier transform spectrum and the pulse width was 6 μs. Pulse repetition times ranged from 1.0 to 4.0 s with delay times of 200 μs. The number of scans ranged from 5000 to 20000.

Details on the equilibrium and kinetic measurements were described in the previous papers.[1,2]

The pD values (= pH-meter readings + 0.40)[9] of D_2O solutions were adjusted with DCl and NaOD, and measured with a Hitachi-Horiba pH-meter Model F-7SS equipped with a micro combined pH electrode. Phthalate and phosphate buffers were used for ^{13}C NMR measurements. Acetate buffers were used for equilibrium and kinetic measurements.

Results and Discussion

^{13}C NMR Spectra of XO and Related Compounds in D_2O. In order to assign ^{13}C signals of XO and Zn(II)–XO, we measured ^{13}C NMR spectra of related compounds of XO, Aurin, PR, *o*-CR, and IDA, at various pD. The structures and the abbreviated nomenclatures of those compounds are shown in Fig. 1. The ^{13}C NMR



Compound	R_1	R_2	R_3	R_4
Aurin	H	H	OH	H
PR	H	SO_3H	H	H
o-CR	CH_3	SO_3H	H	H
XO	CH_3	SO_3H	H	A[a]

a) A = $CH_2N(CH_2COOH)_2$.

Fig. 1. The structures of the triphenylmethanes.

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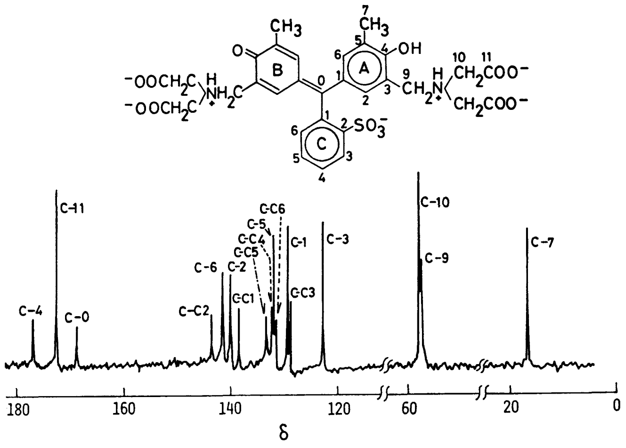

Fig. 2. The ^{13}C NMR spectrum of XO in D_2O at 29°C and pD 6.59.

spectrum of XO is given in Fig. 2.

The central carbon atom of a triphenylmethane skeleton is designated as C-0. The carbon atoms in the A, B, and C ring moieties are designated as C-A*i*, C-B*i*, and C-C*i* ($i=1, 2, \cdots, n$), respectively. In the case of the structural equivalence of the ring moieties, the carbon atoms in these ring moieties are written simply as C-*i*. The ^{13}C signals of the compounds described above were assigned by the peak intensities, the single-frequency off-resonance ^1H decoupling technique, and comparisons of their chemical shifts with those of analogous compounds.[10-12] Data on chemical shifts are summarized in Table 1.

The ^{13}C NMR spectra of Aurin, PR, and *o*-CR show the equivalence between a phenol and a quinonoid ring in neutral and alkaline solutions.[13] Machida *et al.* reported data on the structure of phenolsulfonphthalein dyes, PR, *o*-CR, *etc.*, based on laser-induced Raman spectroscopy. They suggested that phenolsulfonphthalein dyes exist in alkaline solutions as a resonance hybrid of quinonoid and phenolate structures.[14] In the ^{13}C NMR spectra of XO, seventeen peaks were observed in the range of pD 2.0—11.0. This indicates that the A- and the B-ring moieties are equivalent on the NMR time scale irrespective of the existence of a phenolic proton. High intensities of peaks of C-10 and C-11 show the existence of four identical acetate moieties. Ray *et al.* reported that the chemical shifts of the central carbon atom are in the ranges from δ 80 to 82 for para-substituted triphenylmethanols, $(p\text{-}XC_6H_4)_3COH$, and from δ 194 to 212 for the corresponding carbonium ions, $(p\text{-}XC_6H_4)_3C^+$.[15] The central carbon atoms in triphenylmethanols have the tetrahedral configuration, while those in triphenylmethyl cations are reported to be coplanar to the three adjacent ring carbons.[16] For Aurin, PR, *o*-CR, and XO, the signals of C-0 appear in the range from δ 165 to 180, which are comparable to the chemical shifts of C-0 in triphenylmethyl cations.

pD-Dependence of ^{13}C Chemical Shifts for XO. Figure 3 shows plots of values of ^{13}C chemical shifts for seventeen carbon atoms in XO *versus* pD between pD 2.0 and 11.0. C-0, C-1, C-3, C-4, and C-11 undergo significant changes in chemical shifts. Upfield signal shifts for C-0 and C-4, and a small downfield shift for C-10 with an increase in pD observed between pD 2.0 and 4.0 are attributed to the deprotonation at the carboxyl groups. Downfield signal shifts for C-0 and C-4, and an upfield shift for C-1 with an increase in pD observed between pD 5.0 and 8.0 are caused by deprotonation at the phenolic hydroxyl group. Downfield signal shifts for C-3, C-10, and C-11, and an upfield shift for C-0 with an increase in pD observed between pD 9.0 and 11.0 are caused by the deprotonation at $-NH^+-$ groups.[17] For triphenylmethane derivatives, delocalization of charge throughout the π-electron system of the molecule was suggested by Ray *et al.* on the basis of ^{13}C NMR measurements[15] and by

TABLE 1. ^{13}C CHEMICAL SHIFT DATA FOR XO AND RELATED COMPOUNDS IN D_2O AT 29 °C[a, b]

Compound	Aurin	PR	*o*-CR	XO			IDA
pD=	10.63	7.85	9.90	1.99	6.59	11.00	5.92
C-0	179.4(s)	167.6(s)	170.6(s)	166.4(s)	167.3(s)	167.9(s)	
C-1	126.6(s)	123.0(s)	126.4(s)	130.5(s)	129.5(s)	126.5(s)	
C-2	141.7(d)	140.0(d)	140.0(d)	139.1(d)	139.3(d)	139.0(d)	
C-3	121.0(d)	121.9(d)	122.1(d)	121.3(s)	122.2(s)	125.9(s)	
C-4	179.1(s)	176.0(s)	181.6(s)	173.0(s)	175.0(s)	179.6(s)	
C-5			131.2(s)	131.2(s)	131.3(s)	131.4(s)	
C-6			140.2(d)	141.1(d)	140.7(d)	140.3(d)	
C-7			17.2(q)	16.5(q)	16.4(q)	17.0(q)	
C-9				56.1(t)	57.0(t)	57.6(t)	
C-10				55.8(t)	57.5(t)	58.6(t)	49.7(t)
C-11				169.4(s)	171.6(s)	176.7(s)	172.3(s)
C-C1		137.9(s)	138.8(s)	137.3(s)	137.8(s)	138.5(s)	
C-C2		142.7(s)	142.9(s)	142.7(s)	142.8(s)	142.9(s)	
C-C3		128.8(d)	128.9(d)	128.9(d)	128.7(d)	128.6(d)	
C-C4		131.4(d)	131.2(d)	131.5(d)	131.7(d)	131.4(d)	
C-C5		132.2(d)	132.6(d)	132.5(d)	132.9(d)	132.9(d)	
C-C6		130.8(d)	130.5(d)	131.2(d)	131.0(d)	130.7(d)	

a) δ Values; δ(dioxane)=67.4. b) s=Singlet, d=doublet, t=triplet, and q=quartet.

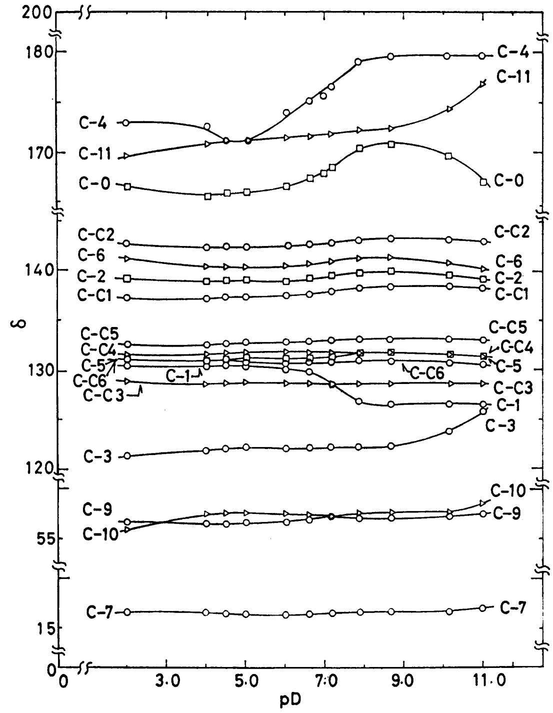

Fig. 3. pD-Dependence of the ^{13}C chemical shifts of XO.

Machida *et al.* from resonance Raman spectroscopic measurements.[14] The large pD-dependence of the chemical shift for C-0 could be explained in terms of the localization-delocalization effect of the π-electron in the molecule.

The chemical shifts of the C-ring carbon atoms were not sensitive to the pD change. In view of this fact, π-electron conjugation in the XO molecule does not spread on the C-ring.

Unexpected distinct pD-dependence of the chemical shift was observed for C-11 in the pD region 9.0—11.0. ^{1}H and ^{13}C chemical shifts are usually influenced by the formation of an intramolecular hydrogen bond.[8] Chapman *et al.* reported in their infrared and ^{1}H NMR studies of ethylenediaminetetraacetic acid and related substances the existence of doubly hydrogen-bonded rings, $-COO^{-}\cdots(NH)^{+}\cdots{}^{-}OOC-$.[19] We infer that the above pD-dependence observed in the chemical shift of C-11 should reflect the existence of such intramolecular hydrogen bonds $-COO^{-}\cdots(NH)^{+}\cdots{}^{-}OOC-$ in XO. A downfield signal shift for C-11 with an increase in pD observed between pD 9.0 and 11.0 would be attributed to the rupture of the hydrogen bonds at the protonated amino groups. Furthermore, a small upfield signal shift for C-4 observed in the pD region 2.5—4.5 would be attributed to the formation of a doubly hydrogen-bonded ring structure, $-COO^{-}\cdots(OH)\cdots{}^{-}OOC-$. Murakami *et al.* suggested the existence of a hydrogen bond between the phenolate oxygen and the proton attached to the amino nitrogen in Semi-Xylenol Orange by spectrophotometric method.[20] However, no pD-dependence was observed in the chemical shift of C-4 for XO in the pD range 9.0—11.0. This result suggests the absence of the hydrogen bond between the phenolate oxygen and the proton attached to the amino nitrogen. From the pD-dependence of chemical shifts of C-0 and C-4, the pK_a value of the phenolic hydroxyl group was determined to be 6.55 at 29 °C. This value is in good agreement with the value derived from the spectrophotometric measurements.[1]

Temperature-dependence of ^{13}C Chemical Shifts for XO. Upon heating a solution of XO buffered at pD 6.93 from 1 to 88 °C, the signals of C-0 and C-4 moved downfield by +0.7 and +1.6 ppm (Table 2). The feature of the temperature-dependence of the chemical shifts of C-0 and C-4 was similar to that of the pD-dependence of the chemical shifts of the same carbon atoms in the pD range 5.0—8.0. Since the pD-dependence of the chemical shifts of C-0 and C-4 is caused by the protonation-deprotonation equilibrium of the phenolic hydroxyl group, we conclude that the temperature-dependence of the chemical shifts for the free ligand XO is also caused by temperature-dependent protonation-deprotonation at the phenolic hydroxyl group.

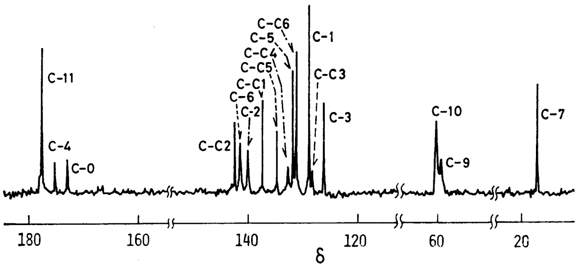

Fig. 4. The ^{13}C NMR spectrum of the Zn(II)–XO in D_2O at 29 °C and at pD 3.88. $[Zn(II)]_0 = 1.7$ mol dm^{-3}. $[XO]_0 = 0.17$ mol dm^{-3}.

^{13}C NMR Spectrum of Zn(II)–XO Complex and its pD-Dependence. ^{13}C NMR spectra of Zn(II)–XO complex were measured in the pD range 1.9—5.5 and at 29 °C using D_2O solutions containing a ten-fold excess of Zn(II) ion over the ligand. Figure 4 shows ^{13}C NMR spectrum at pD 3.88. Around pD 2.0 the signals of the carbon atoms, except for the C-ring carbon atoms, were broadened. Seventeen peaks resulting from the predominance of 2 : 1 Zn(II)–XO complex having coordinated carboxylate and amino groups were

TABLE 2. CHEMICAL SHIFTS OF C-0 AND C-4 FOR Zn(II)–XO AND FREE XO[a] AT VARIOUS pD VALUES[b] AND TEMPERATURES

T/°C			1	29	88
Zn(II)–XO	pD=3.88[c]	C-0	173.8	174.0	175.5
		C-4	176.9	176.8	180.1
	pD=5.46	C-0		176.0	
		C-4		182.5	
XO	pD=6.93[d]	C-0	167.3	167.6	168.0
		C-4	174.8	175.5	176.4
	pD=8.24	C-0		170.7	
		C-4		179.5	

a) δ Values; δ(dioxane)=67.4. b) At 29 °C. c) Phthalate buffers were used. d) Phosphate buffers were used.

observed at pD 3.88 (Fig. 4). At pD 5.46, more than nineteen peaks were observed, indicating that the formation of 1 : 1 Zn(II)–XO complex is not negligible.[21] Signals of C-0 and C-4 were observed at δ 174.0 and 176.3 at pD 3.88, and δ 176.0 and 182.5 at pD 5.46, respectively (Table 2). Both signals of C-0 and C-4 were shifted to lower fields with an increase in pD of the solution. The features of pD-dependence of chemical shifts of C-0 and C-4 for Zn(II)–XO in the pD range 3.8—5.5 were quite similar to those for the free ligand XO in the pD range 5.0—8.0. Therefore, the pD-dependence of chemical shifts of C-0 and C-4 observed for Zn(II)–XO was ascribed to the deprotonation of a phenolic hydroxyl group accompanied with coordination to the central Zn(II).

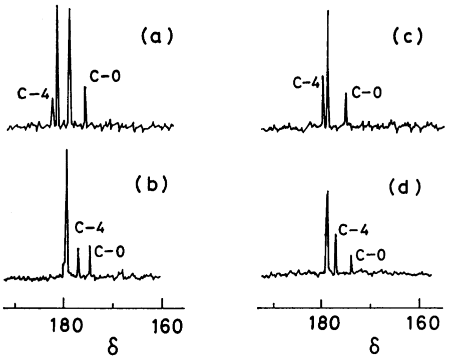

Fig. 5. pD- and temperature-dependence of the chemical shifts of C-0 and C-4 for Zn(II)–XO in D_2O. At 29 °C and at pD 5.46 (a) and 3.88 (b). At pD 3.88 and at 88 (c) and 1 °C (d). Phthalate buffres were used for (c) and (d).

Temperature-dependence of ^{13}C Chemical Shifts for Zn(II)–XO. ^{13}C NMR spectra of Zn(II)–XO were measured at various temperatures in the pD region where remarkable pD-dependences of the chemical shifts of C-0 and C-4 were observed.[22] Signals of C-0 and C-4 moved downfields by +1.7 and +3.2 ppm upon heating a solution of Zn(II)–XO buffered at pD 3.88 from 1 to 88 °C (Table 2). The feature of the temperature-dependences of chemical shifts of C-0 and C-4 (Figs. 5(a) and (b)) was similar to that of the pD-dependences of chemical shifts of the same carbon (Figs. 5(c) and (d)). This fact indicates that the temperature-dependences of the chemical shifts of C-0 and C-4 for Zn(II)–XO is caused by temperature-dependent protonation-deprotonation of a phenolic hydroxyl group in the coordinated ligand.

Spectrophotometric and Temperature-jump Studies. Figure 6 shows the temperature-dependence of the visible absorption spectra of an aqueous solution of Zn(II)–XO at pH 3.97 in the presence of a ten-fold excess of the metal ion over the ligand. The absorption spectrum changes reversibly with a distinct isosbestic point at 492 nm. As the temperature rises the absorbance at 450 nm decreases accompanied with a large increase in the absorbance at 572 nm. The feature of the temperature-dependence of the absorption spectra at a constant pH was quite similar to that of the pH-dependence of the absorption spectra at a constant temperature. These facts clearly indicate that the observed thermochromism of Zn(II)–XO is primarily due to the temperature-dependence of the protolytic equilibrium (1).

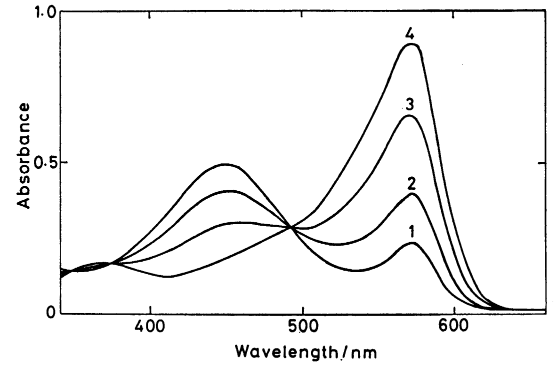

Fig. 6. Temperature-dependence of the absorption spectra of the Zn(II)–XO. At 5 (1), 24 (2), 45 (3), and 69 °C (4). $[\mathrm{Zn(II)}]_0 = 2.0\times10^{-4}$ mol dm^{-3}. $[\mathrm{XO}]_0 = 2.0\times10^{-5}$ mol dm^{-3}. $I = 0.1$ mol dm^{-3} ($NaClO_4$). At pH=3.97±0.02.

Upon heating a solution of Zn(II)–XO complex at pH 3.97 from 15 to 35 °C, the absorbance at 572 nm increased by so large as 40%, whereas the absorbance at 580 nm of the free ligand at pH 6.40, near the pK_a value of the phenolic proton of the free ligand XO, increased only by 19% for the same temperature-rise. The increments in the chemical shifts of C-0 and C-4 for Zn(II)–XO at pD 3.88 were 1.0 and 1.9%, respectively, for temperature-rise from 1 to 88 °C, and those for the free ligand at pD 6.93 were 0.4% and 0.9% for the same temperature-rise.[23] In both spectrophotometric and ^{13}C NMR measurements, the increments of the quantities measured for the Zn(II) complex were twice as large as those for the free ligand upon heating the solutions.

Temperature-jump studies were carried out for Zn(II)–XO. A relaxation signal of an increasing absorbance at 572 nm observed in 5—10 μs region is attributed to the protolytic reaction of a phenolic hydroxyl group. The value of the rate constant for the dissociation of a phenolic proton in the complex was estimated to be 2.3×10^5 s^{-1}. This value was in the same order of magnitude as that for Cu(II)–XO.[1]

Considering the equilibrium and the kinetic data, we concluded that the temperature-dependence of the chemical shifts of C-0 and C-4 for Zn(II)–XO is primarily ascribed to the temperature-dependence of protolytic equilibrium (1).

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22) Changes in all chemical shift values upon heating unbuffered solutions of both XO and Zn(II)–XO were similar to the changes in chemical shifts with a decrease in pD of the same solutions. At 88 °C the spectrum of an unbuffered XO solution at pD 6.42 showed two new peaks assigned to C-10 and C-11 of free IDA (Table 2) in the same pD region.

23) Increases in ^{13}C chemical shifts were smaller than those expected because of the incomplete buffer action in the solutions. Upon heating from 1 to 75 °C the pH-meter reading decreased from 3.75 to 3.10 for Zn(II)–XO and from 6.51 to 6.06 for the free ligand XO.