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SYNTHESIS OF A NEW TRIPHENYLMETHANE COMPLEXON

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A new type triphenylmethane complexon containing an iminodiacetic acid and a pyridinium group incorporated in an o-Cresol Red skeleton was synthesized. The new complexon was found to be useful as a metallochromic indicator for the complexometric titrations of multivalent metal ions, Ga^{3+}, In^{3+}, Tl^{3+}, Fe^{3+}, and Zr^{4+} ions.

Xylenol Orange (XO), one of the well-known triphenylmethane complexons (TPMC), has been proved to be an excellent metallochromic indicator for the complexometric determinations of many metal ions even in acidic media, but the determinations of some bivalent and multivalent metal ions with this indicator are not always successful because of the too high stabilities of the metal chelates.1) In the complexometric titrations of multivalent metal ions with a TPMC indicator, the use of an indicator forming complexes less stable than those of XO is essential.

In the present communication we designed the synthesis of a new metallochromic indicator along this line. The synthesized new TPMC was found to form complexes of reasonably reduced stabilities with multivalent metal ions as compared with XO, giving a sharp color change at the end point.

Synthesis of the new TPMC. o-Cresol Red (o-CR, 1.91 g) dissolved in pyridine (5.0 cm^3) was mixed with iminodiacetic acid (1.33 g) and NaOH (2.5 g) dissolved in acetic acid (45 cm^3), and kept at 90 °C. To this solution 37% formaldehyde (1 cm^3) was added drop by drop. The reactions were monitored by a high-performance liquid chromatography (HPLC) for analytical purpose (see Fig. 1). In the initial stage of the reaction the formation of Semi-Xylenol Orange (SXO) was observed, which was followed by the formation of XO. After the yield of SXO and XO reached maxima the yields of the new TPMC and an unknown product gradually increased with the lapse of time. The final reaction mixture was purified beforehand through a cellulose column using an eluent, 1-butanol saturated with 25% aqueous acetic acid/28% aqueous ammonia (100/1, v/v).2) The pre-purified new TPMC was further purified by HPLC through a Bondapak C_{18} Porasil column using an eluent, 7% aqueous acetic acid/methanol (7/3, v/v).3) The new TPMC was readily precipitated as fine crystals from this mixed solvent, and could be purified by repeated recrystallization. The purified sample of the new TPMC was converted to a free acid form through a cation-exchange resin in the H-form. Yield: ca. 30%. Found: C, 60.74; H, 4.98; N, 4.37; S, 5.18%, C/N, 13.9. Calcd for $C_{32}H_{30}N_2SO_9 \cdot H_2O$: C, 60.37; H, 5.07; N, 4.40; S, 5.03%, C/N = 13.7.

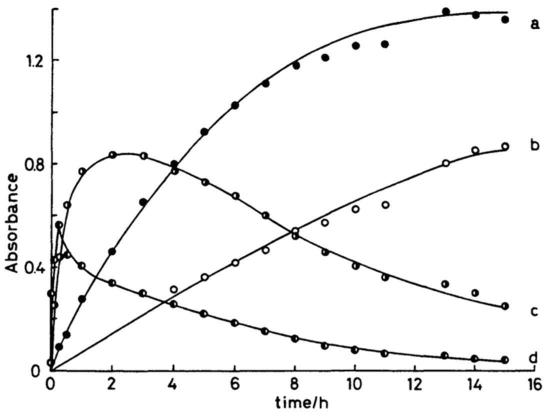

Fig. 1. The reactions monitored by HPLC. a: The new TPMC, b: an unknown product, c: XO, and d: SXO. The reaction mixture (0.2 mm^3) at each time was passed through a column of μ-Bondapak C_{18} Porasil, eluted with a solvent, 7% aq. acetic acid/methanol (6/4, v/v), and analyzed at 436 nm.

IR spectra of the new TPMC (in nujol) show absorption bands at 3014 (m), 1521 (s), 1172 (s), 782 (w), 753 (m), and 688 (m) cm^{-1} which are not observed for XO. These bands were assigned to the pyridine substituent in the molecule.[4,5] The bands at 753 and 688 cm^{-1} are characteristic for the adjacent five hydrogen atoms,[5,6] indicating that in the new TPMC the pyridine molecule is incorporated through a bond at a nitrogen atom.

Values of the chemical shifts and coupling constants for ^1H NMR spectra in Fourier transform mode of the new TPMC in D_2O are summarized in Table 1. Difference in the values of the chemical shifts for methyl groups indicates that the benzene rings A and B in the molecule are not equivalent. The integrated intensities and the values of the coupling constants of the ^1H NMR signals correspond to the presence of five ring-protons, i.e., α-, β-, and γ-protons in the pyridine substituent. This fact also suggests the bond formation at the nitrogen atom of the pyridine substituent in the new TPMC. Furthermore, the limited solubility in polar solvents of the new TPMC suggests the presence of a sort of intramolecular interaction between the incorporated pyridinium group and the sulfonate group in the benzene ring C.

From these results the following structure is proposed for the new TPMC.

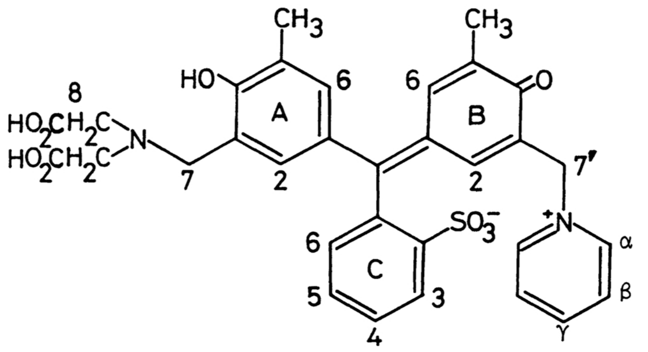

Fig. 2. The new TPMC: $C_{32}H_{30}N_2SO_9$.

TABLE 1. ^{1}H NMR DATA FOR THE NEW TPMC IN D_2O AT 60 °C. pD∿0. (δ/ppm from DSS)[a]

2.08 (s, A-CH_3), 2.15 (s, B-CH_3), 4.28 (s, 8-H), 4.59 (s, 7-H), 5.67 (s, 7'-H), 7.18-7.3 (m, C6-H), 7.3-7.40 (m, A2-H, B2-H, A6-H, B6-H), 7.63-7.74 (m, C3-H, C4-H), 7.95-8.07 (m, C3-H), 8.04 (2d, β-H, J, 7.7, 6.8 Hz), 8.54 (n, γ-H, J, 7.7, 1.4 Hz), 8.86 (q, α-H, J, 6.8, 1.4 Hz)

a) s: singlet, d: doublet, q: quartet, n: nonet, and m: multiplet.

Figure 3 shows the pH-dependence of the absorbance at 577 nm, the absorption maximum of the new TPMC; the values of λ_{max} remained unchanged for the dissociation of a phenol proton and an amine proton of the iminodiacetate group. An increase in absorbance in the lower pH region and a subsequent decrease at higher pH correspond to the dissociation of the phenol proton and the amine proton, respectively. Differed from the case of XO,[7)] no change in absorbance was observed above pH 11, indicating the presence of only one iminodiacetic acid group in a molecule of the new TPMC. The acid-dissociation constants for the phenolic and the amine proton of the new TPMC and the molar absorptivities were determined to be $pK_a^{LH_2} = 6.39 \pm 0.03$ for $LH_2 \rightleftharpoons LH + H$ and $pK_a^{LH} = 10.47 \pm 0.03$ for $LH \rightleftharpoons L + H$ (charges are omitted), and $\varepsilon_{577nm}^{LH} = (7.12 \pm 0.09) \times 10^4$ and $\varepsilon_{577nm}^{L} = (5.63 \pm 0.10) \times 10^4$ mol^{-1} dm^3 cm^{-1}, at I = 0.1 mol dm^{-3} ($NaClO_4$) and at 25 °C.

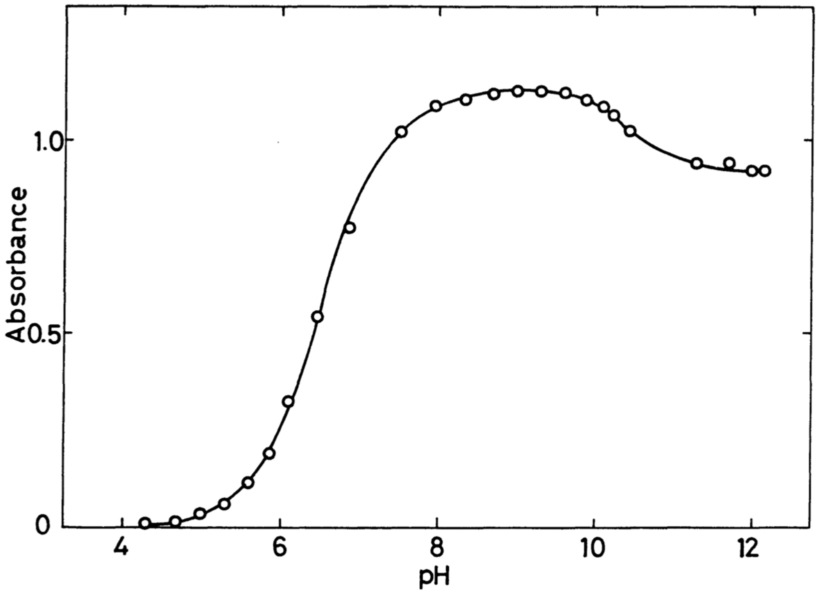

Fig. 3. pH-Dependence of the absorbance at 577 nm of the new TPMC. [TPMC] = 1.60 x 10^{-5} mol dm^{-3}, I = 0.1 mol dm^{-3} and at 25 °C.

Complexometric titrations of multivalent metal ions using the new TPMC as an indicator. Preliminary complexometric titrations of tervalent and quadrivalent metal ions, Ga^{3+}, In^{3+}, Tl^{3+}, Fe^{3+}, and Zr^{4+}, using the new TPMC as an indicator were successfully carried out. As the new TPMC is very stable in water, the aqueous solution of the new TPMC (ca. 1%, w/w) was used as an indicator. Table 2 shows the pH ranges and the color changes at the end point for the successful direct complexometric determinations of the multivalent metal ions. These data indicate that the new TPMC is useful as an metallochromic indicator for the complexometric determinations of the multivalent metal ions. The syntheses of a series of similar new TPMC indicators having pyridine derivatives incorporated are now in progress.

TABLE 2. pH RANGES FOR THE SUCCESSFUL COMPLEXOMETRIC TITRATIONS USING THE NEW TPMC AND THE COLOR CHANGES AT THE END POINT

Metal ion	pH range	Color change
Ga^{3+}	2.0-4.5[a)]	orange to pale yellow
In^{3+}	2.0-4.5[b)]	orange to pale yellow
Tl^{3+}	2.0-5.0	orange to pale yellow
Fe^{3+}	1.5-3.5[b)]	violet to yellow
Zr^{4+}	2 mol dm^{-3} $HClO_4$-pH 1.5[a)]	violet to yellow

a) At ca. 90 °C. b) At ca. 60 °C.

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