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On 1-Phenyl-3-Methyl-4-Benzoylthiopyrazol-5-One As an Analytical Reagent

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A monothio derivative of 1-phenyl-3-methyl-4-benzoylthiopyrazol-5-one and its metal chelates were synthesized and characterized through some spectroscopic measurements. Zinc and cadmium ions were readily extracted into benzene at a lower pH region than 1-phenyl-3-methyl-4-benzoylpyrazol-5-one.

KEY WORDS: 1-Phenyl-3-methyl-4-benzoylthiopyrazol-5-one/
Solvent extraction/

INTRODUCTION

1-Phenyl-3-methyl-4-benzoylpyrazol-5-one (HPMBP) and its derivatives have been extensively employed for the solvent extraction reagent. In the previous papers, the authors have investigated the extraction behaviors of europium and barium^{1,2)}, and the synergistic extraction of alkaline earths.³⁾

It is known that replacement of oxygen to sulfur as a donor atom often gives some interesting properties. Monothio β -diketones were first synthesized by Chaston *et al.*,⁴⁾ and many investigations have been made on the solvent extraction and the colorimetric determination of metal cations.

The present paper will report on the synthesis of a mono-thio-derivative of HPMBP, 1-phenyl-3-methyl-4-benzoylthiopyrazol-5-one (HSPMBP), and its metal chelates, together with the characterization of the compounds and some applications to the solvent extraction.

EXPERIMENTAL

MATERIALS

Synthesis of HSPMBP — HSPMBP was synthesized according to the similar method described in the literatures.^{4~6)} Dry hydrogen chloride gas was bubbled through a solution of HPMBP in absolute ethanol for twenty minutes at 0°C, followed by passing dry hydrogen sulfide gas for one hour. On passing the latter, the yellow solution turned dark red. Then the solution was poured into appropriate amount of ice, and the yellow product precipitated immediately. The product was collected

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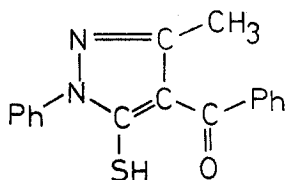


Fig. 1. 1-phenyl-3-methyl-4-benzoylthiopyrazol-5-one.

by filtration, washed with water, dried in a desiccator and recrystallized from ethanol. Yellow needles were obtained in 76% yield. The structural formula is shown in Fig. 1.

Synthesis of metal chelates—To metal acetate dissolved in ethanol, double the molar quantity of HSPMBP ethanol solution was added. The product was precipitated from the reaction mixture, then filtered, washed and dried. The chelates were recrystallized from benzene.

APPARATUS

Radioactivity measurements were carried out with a Metro Electronics NaI (TI) well-type scintillation counter (44.5 mm diameter, 50.5 mm depth), Model PbW-6, equipped with a Metro automatic scaler, Model SS-1061H. Atomic absorption measurements were made with a Japan Jarrell-Ash Model AA-781 spectrometer. Other instrumentation included a Hitachi-Horiba pH meter (Model F-7ss), a Hitachi 323 recording spectrophotometer (for spectra) and Hitachi 139 spectrophotometer (for absorbance measurements) with 1 cm cells.

EXTRACTION PROCEDURE

The procedure was almost the same as described previously.¹⁾ The distribution ratio of cadmium was determined by atomic absorption spectrometry and that of zinc by radiometry.

RESULTS AND DISCUSSION

The analytical data of the ligand, HSPMBP, and its metal chelates are given in Table I. Although HSPMBP is a sulfur-containing ligand such as thiothenoyl-trifluoroacetone and thiodibenzoylmethane, it was found to be a very stable reagent. Some monothio β -diketones do not always have a constant melting point. It shows that some difficulties may arise in synthesis, isolation and purification owing to their unstableness. HSPMBP has a constant melting point of 106°C through three times of synthesis. PMR and UV measurements indicate the stability of the ligand more than three months' preservation in a sample tube and more than two weeks' in cyclohexane solution both at a room temperature.

Fig. 2 and 3 show the absorption spectra of HPMBP, HSPMBP and the metal chelates of HSPMBP, and these are summarized in Table II. The absorption spectrum of HSPMBP agrees with the data of Uhlemann *et al.*,⁷⁾ the absorption maximum at the longest wavelength is observed at 366 nm, which has a considerably high molar extinction coefficient ($\epsilon = 2.11 \times 10^4$).

Table I. Elemental analysis of the compounds

| Compound | Elemental analysis | | | mp. (°C) | |
|-------------------------|--------------------|---|------|----------|---------|
| | Calc. found | C | H | | N |
| HSPMBP | 69.36 | | 4.79 | 9.52 | 106 |
| | 69.54 | | 4.77 | 9.28 | |
| Zn (SPMBP) ₂ | 62.62 | | 4.02 | 8.59 | 278 |
| | 62.82 | | 4.03 | 8.64 | |
| Ni (SPMBP) ₂ | 63.27 | | 4.06 | 8.68 | 272 |
| | 63.42 | | 4.18 | 8.83 | |
| Cu (SPMBP) ₂ | 62.80 | | 4.03 | 8.62 | 224 |
| | 63.00 | | 4.02 | 8.55 | |
| Pb (SPMBP) ₂ | 51.43 | | 3.16 | 7.06 | — |
| | 51.71 | | 3.31 | 7.01 | |
| Cd (SPMBP) ₂ | 58.66 | | 3.76 | 8.02 | 270 |
| | 58.40 | | 3.63 | 7.93 | |
| Hg (SPMBP) ₂ | 51.87 | | 3.33 | 7.12 | 246~247 |
| | 52.11 | | 3.27 | 6.75 | |

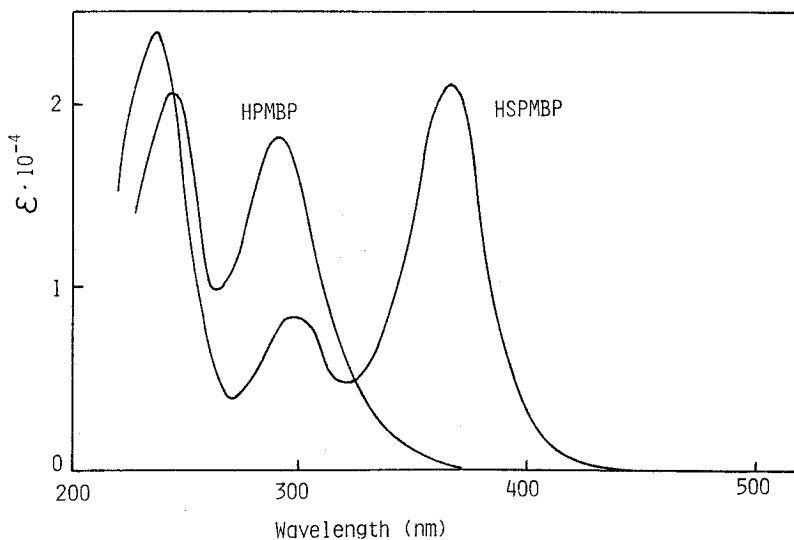


Fig. 2. Absorption spectra of HPMBP and HSPMBP in cyclohexane solution.

IR spectrum of the ligand was obtained in KBr disk. Strong band at 1592 cm^{-1} and medium band at 1266 cm^{-1} are assigned to C=O and C=S stretching, respectively. PMR spectrum was recorded in CDCl_3 solution using TMS as an internal standard. HSPMBP shows a singlet at 14.04 ppm due to O-H group instead of a C-H proton absorption. This indicates that HSPMBP exists as an enol form in CDCl_3 . A multiplet centered at 5.4 ppm and a singlet at 1.76 ppm are assigned to two phenyl groups and methyl protons, respectively.

The solvent extractions with HSPMBP of zinc and cadmium ions were also examined. When the metal ion, the ligand and the distribution ratio of the metal

Table II. Ultraviolet and visible spectra of HSPMBP and chelates

| Compound | Color | λ_{\max} | $\epsilon (\times 10^{-4})$ |
|-------------------------|---------------|------------------|-----------------------------|
| HSPMBP | Yellow | 236 | 2.38 |
| | | 300 | 0.83 |
| | | 366 | 2.11 |
| Zn (SPMBP) ₂ | Bright yellow | 359 | 3.82 |
| Ni (SPMBP) ₂ | Reddish brown | 327 | 3.35 |
| | | 420 | 1.39 |
| Cu (SPMBP) ₂ | Dark brown | 354 | 2.93 |
| Pb (SPMBP) ₂ | Yellow | 368 | 2.55 |
| Cd (SPMBP) ₂ | Pale yellow | 358 | 3.85 |
| Hg (SPMBP) ₂ | Orange | 303 | 1.91 |
| | | 345 | 2.28 |

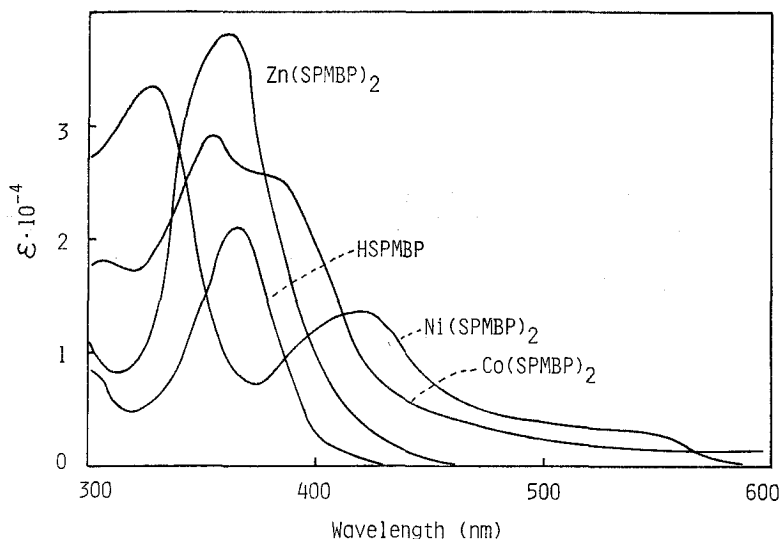
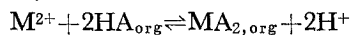


Fig. 3. Absorption spectra of HSPMBP chelates in benzene solution.

ion are denoted by M^{2+} , HA and D, the extraction equilibrium and the extraction constant, K_{ex} , can be written as follows.



$$K_{ex} = \frac{[MA_{2,org}][H^+]^2[M^{2+}]^{-1}}{[HA]_{org}^{-2}} = D[H^+]^2[HA]_{org}^{-2}$$

and

$$\log K_{ex} = \log D - 2pH - 2 \log [HA].$$

The subscript org denotes the species in organic solvent. Fig. 4 shows the log D vs. pH plots in the extraction of zinc and cadmium. Both slopes of the plots are almost two, the theoretical value. The dependence of D against the concentration of the ligand in the extraction of zinc was also examined and shown in Fig. 5. The slope, which expresses the number of the ligand in the extracted complex, is almost two. It shows that side reactions such as dimerization or polymerization of the ligand do not occur in this ligand concentration range. Thus zinc and cadmium are ex-

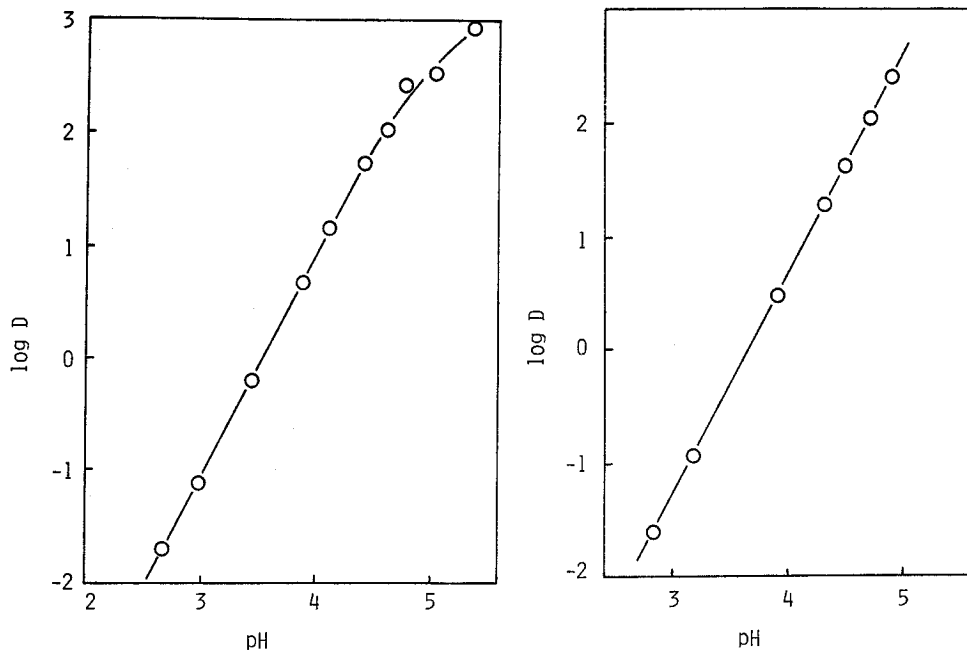


Fig. 4. (I) Logarithm of the distribution ratio of Zn(II) as a function of pH. Org. phase: 1×10^{-3} M HSPMBP in benzene, aq. phase: 0.1 M NaClO_4 . (II) Logarithm of the distribution ratio of Cd(II) as a function of pH. Org. phase: 1×10^{-2} M HSPMBP in benzene, aq. phase: 0.1 M NaClO_4 .

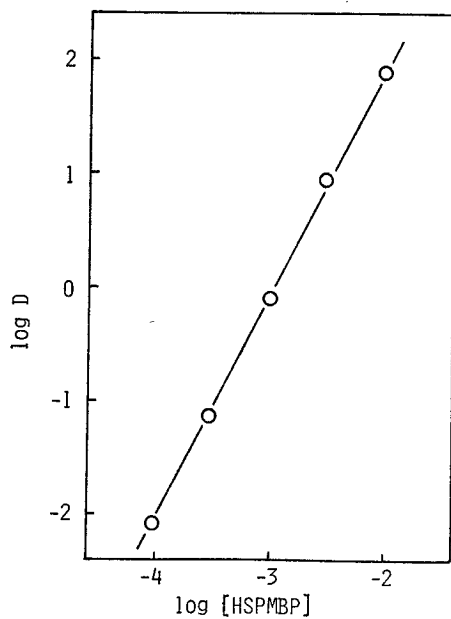


Fig. 5. Effect of HSPMBP concentration on the extraction of Zn(II). Org. phase: HSPMBP 1×10^{-4} – 1×10^{-2} M in benzene, aq. phase: NaClO_4 0.1 M, at pH 3.50.

tracted as $\text{Zn}(\text{SPMBP})_2$ and $\text{Cd}(\text{SPMBP})_2$. The calculated value of $\log K_{\text{ox}}$ is -1.12 for zinc and -3.22 for cadmium. When HPMBP is used, $\log K_{\text{ox}}$ is -5.14 for zinc and -8.52 for cadmium.⁸⁾

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