

Electrochemical Behavior of Some Metal Complexes of 1-phenyl-3-methyl-4-benzoyl-5-pyrazolone and Its Acyl Derivatives in Non-aqueous Solvents

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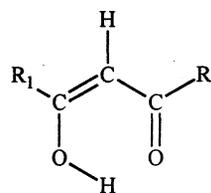
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The complexes of divalent metals (Ni^{II}, Cu^{II}, Mn^{II}, Co^{II}, Cd^{II}), trivalent metals (Fe^{III} and Cr^{III}), lanthanide metals (La^{III}, Pr^{III}, Eu^{III}, Lu^{III}) with 1-phenyl-3-methyl-4-benzoyl-5-pyrazolone (Hpmbp) and the Fe^{III} complexes with its acyl derivatives (HpmC_n) were prepared and their electrochemical behavior was investigated. The cyclic voltammogram of each lanthanide complex with Hpmbp in *N,N*-dimethylformamide gave an irreversible one-electron oxidation peak. In the case of the divalent metal complex, an irreversible oxidation peak was observed for each complex in acetonitrile. The Cu^{II} and Cd^{II} complexes also exhibited an irreversible reduction peak at the cathodic potential sweep with an anodic stripping peak during the reverse anodic sweep. The Fe^{III} and Cr^{III} complexes with Hpmbp and Fe^{III} complex with HpmC-*n* gave quasi-reversible reduction peaks corresponding to the reduction of the metal in dichloromethane. Linear correlation was established between the reduction potentials of Fe^{III} pyrazolonato complexes and the pK_a value of the ligands.

Keywords: electrochemistry; metal complexes; pyrazolonato complexes; β -diketonato complexes; cyclic voltammetry; lanthanide metals

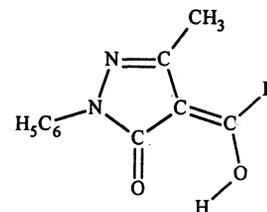
INTRODUCTION

1-Phenyl-3-methyl-4-benzoyl-5-pyrazolone (Hpmbp) and its acyl derivatives (HpmC_n) are β -diketonates whose structures are shown below. They are very useful reagents for solvent extraction of metal ions. The acid dissociation constant (K_a) of Hpmbp is larger than that of acetylacetone. It is therefore possible to extract metal ions in acidic media with Hpmbp [1, 2]. The pyrazolone derivatives form stable metal complexes but the resulting complexes have never been characterized electrochemically unlike the well-studied β -diketonato complexes.



β -diketone
Hacac (acetylacetone): R₁ = R₂ = CH₃

Derivative of Pyrazolone
Hpmbp: R₃ = C₆H₅
HpmC_n: R₃ = (CH₂)_nCH₃ (n = 1-9)



In this study, the electrochemical behavior of the complexes of divalent metals (Ni^{II} , Cu^{II} , Mn^{II} , Co^{II} , Cd^{II}), trivalent metals (Fe^{III} and Cr^{III}), lanthanide metals (La^{III} , Pr^{III} , Eu^{III} , Lu^{III}) with Hpmbp and the Fe^{III} complexes with HpMC n were investigated in dichloromethane, *N,N*-dimethylformamide, or acetonitrile.

EXPERIMENTAL

Voltammetric analysis. Voltammetric analysis was carried out using the Fuso Electrochemical System (Polarograph Model 312 and Potential Sweep Unit HECS 321B) coupled with the Riken-Denshi X-Y recorder [3]. A platinum disk with diameter of 2.0 mm was used as the working electrode for voltammetric experiments. The auxiliary electrode was also a platinum disk electrode. The Ag/AgCl reference electrode was connected to the test solution through a salt bridge with a Vycor plug filled with the background solution. All the potentials were measured against the reference electrode. When the potentials were compared to those in different solvents, the potential was determined against the half-wave potential of the Fc/Fc^+ couple as an internal standard. For controlled-potential electrolysis, a Fuso Coulometric Model 343 was attached to the electrochemical system. All voltammetric analyses were carried out at 25°C.

Considering the solubility of the complexes, *N,N*-dimethylformamide was used for the measurement of divalent metal complexes and lanthanide complexes while dichloromethane and acetonitrile were used for the measurement of the trivalent metal complexes.

Materials. The purification of acetonitrile and *N,N*-dimethylformamide for electrochemical work were carried out as described in [3]. Dichloromethane was purified through the distillation of the reagent grade solvent over P_2O_5 . The supporting electrolyte was special polarographic grade tetrabutylammonium perchlorate (TBAP) purchased from Nakarai Chemicals, Ltd. For the synthetic experiments, commercially available reagent grade solvents, and chemicals were used.

Preparation of the complexes. The complexes of $[\text{M}^{\text{II}}(\text{pmbp})_2]$ ($\text{M} = \text{Ni}^{\text{II}}$, Cu^{II} , Mn^{II} , Co^{II} , Cd^{II}) and $[\text{M}^{\text{III}}(\text{pmbp})_3]$ ($\text{M}^{\text{III}} = \text{Fe}$ and Cr) were prepared as follows. The metal nitrates (except MnCl_2 and CuSO_4 , for $[\text{Mn}^{\text{II}}(\text{pmbp})_2]$ and $[\text{Cu}^{\text{II}}(\text{pmbp})_2]$, respectively) were dissolved in water and the pH of the solution was adjusted to pH 4 to 5 by the addition of sodium acetate solution. Then, the methanol solution of Hpmbp was added to the solution of the metal salt. The ratio of Hpmbp to the metal was two for $[\text{M}^{\text{II}}(\text{pmbp})_2]$ and three for $[\text{M}^{\text{III}}(\text{pmbp})_3]$. The solution was stirred for 1 h at 70°C to 80°C in the water bath. During stirring, methanol was evaporated off and then a crystalline precipitate was obtained. It was collected by filtration and washed with water. After drying, it was washed several

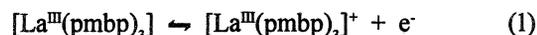
times with hexane in order to remove unreacted Hpmbp. In the case of iron complexes, further purification was carried out by recrystallization from acetone.

For the preparation of lanthanide complexes, lanthanide oxide was dissolved in nitric acid and then the pH of the solution was adjusted to about 4. The succeeding preparation steps were the same as those for $[\text{M}^{\text{II}}(\text{pmbp})_2]$ and $[\text{M}^{\text{III}}(\text{pmbp})_3]$.

The results of elemental analysis of $[\text{Fe}(\text{pmbp})_3]$ is as follows: Calcd. for $\text{FeC}_{51}\text{H}_{39}\text{O}_6\text{N}_6$: C, 69.00; H, 4.43; N, 9.47%. Found: C, 68.28; H, 4.39; N, 9.39%. While for elemental analysis of $[\text{Cr}(\text{pmbp})_3]$: Calcd. for $\text{CrC}_{51}\text{H}_{39}\text{O}_6\text{N}_6$: C, 69.30; H, 4.45; N, 9.51%. Found: C, 69.07; H, 4.29; N, 9.31%.

RESULTS AND DISCUSSION

Lanthanide complexes. The cyclic voltammogram of $[\text{La}^{\text{III}}(\text{pmbp})_3]$ in *N,N*-dimethylformamide gave a one-electron oxidation peak without a corresponding reduction peak (Fig. 1). This result indicates the occurrence of a chemical reaction following the electron transfer:



The potential difference between the peak (E_p) and the half-peak point ($E_{p/2}$) (the potential at the half height of the peak current) of the oxidation peak was 90 mV, indicating the quasi-reversible nature of the electron transfer. The oxidation site may be the pmbp ligand because the Hpmbp showed an irreversible oxidation peak at 0.78 V.

The cyclic voltammograms of the complexes of $[\text{Pr}^{\text{III}}(\text{pmbp})_3]$, $[\text{Eu}^{\text{III}}(\text{pmbp})_3]$, and $[\text{Lu}^{\text{III}}(\text{pmbp})_3]$ were similar to that of $[\text{La}(\text{pmbp})_3]$. Although the reversible reduction of $[\text{Eu}^{\text{III}}(\text{acac})_3]$ at the dropping mercury electrode has been re-

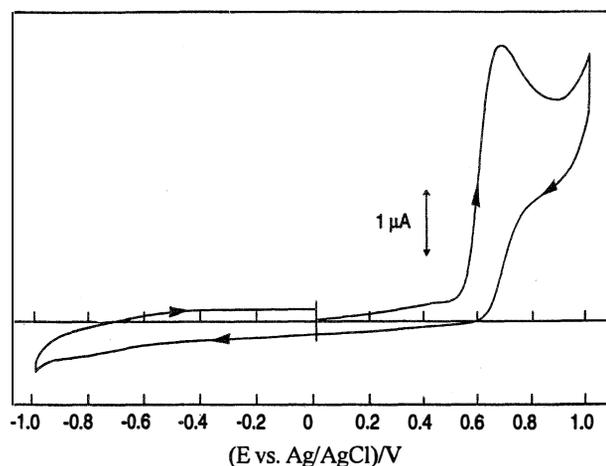


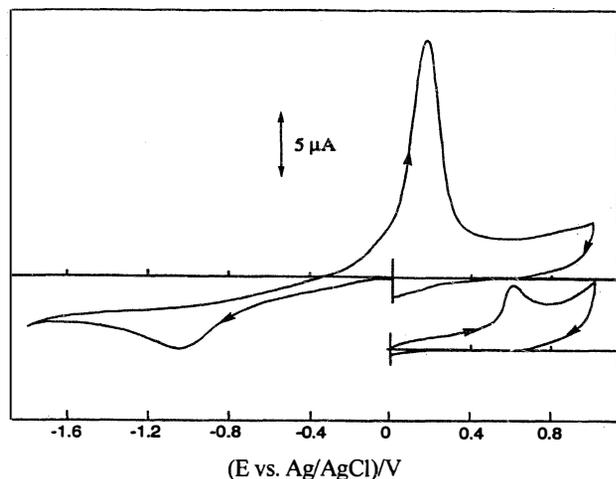
Fig. 1. The cyclic voltammogram of $[\text{La}(\text{pmbp})_3]$ in 0.1 mol dm^{-3} TBAP-*N,N*-dimethylformamide at 25°C. Scan rate is 100 mV/s.

Table 1. Anodic peak potentials (E_p) and potential difference between E_p and $E_{p/2}$ of the cyclic voltammograms of the lanthanide complexes.

Complex	E_p/V	$(E_p - E_{p/2})/mV$
[La ^{III} (pmbp) ₃]	0.67	80
[Pr ^{III} (pmbp) ₃]	0.55	79
[Eu ^{III} (pmbp) ₃]	0.65	70
[Lu ^{III} (pmbp) ₃]	0.65	83

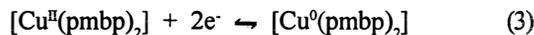
Table 2. The anodic and cathodic peak potentials (E_{pa} and E_{pc}) of the cyclic voltammograms of the divalent metal complexes.

Complex	E_{pc}/V	E_{pa}/V
[Cu ^{II} (pmbp) ₂]	-1.05	0.72
[Cd ^{II} (pmbp) ₂]	-1.27	0.69
[Ni ^{II} (pmbp) ₂]	-----	0.66
[Co ^{II} (pmbp) ₂]	-----	0.67
[Mn ^{II} (pmbp) ₂]	-----	0.70

**Fig. 2.** The cyclic voltammograms of [Cu(pmbp)₂] in 0.1 mol dm⁻³ TBAP-N,N-dimethylformamide at 25°C. Scan rate is 100 mV/s.

ported in the same media [4], no reduction peak was observed. The peak potentials (E_p) and the potential difference between E_p and $E_{p/2}$ for the lanthanide complexes are tabulated in Table 1. There was no large difference between the peak potentials. This behavior indicates similarity of the electrochemical properties of the four lanthanide central metal atoms and oxidation involving the ligand.

Divalent metal complexes. The cyclic voltammograms of [Cu^{II}(pmbp)₂] is shown in Fig. 2. The ill-defined reduction peak without corresponding oxidation peak was observed at the cathodic potential sweep. At the following reversed anodic sweep, the sharp and large oxidation peak appeared. This behavior can be explained by the following homogeneous chemical reactions. During the cathodic sweep, the complex was reduced (Eq. 3) and the metal copper was deposited on the electrode surface (Eq. 4). Then, when the potential was switched back to the anodic direction, anodic stripping of metal copper took place (Eq. 5).



[Cd^{II}(pmbp)₂] also showed similar cyclic voltammetric behavior, although the other divalent metal complexes ([Ni^{II}(pmbp)₂], [Co^{II}(pmbp)₂] and [Mn^{II}(pmbp)₂]) did not show any reduction peak within the potential window (-1.6 V). Peak potentials of the complexes are shown in Table 2. In acetonitrile, the bis(acetylacetonato) divalent metal complexes showed irreversible reduction peaks [5]. Sock *et al.* reported that the reduction potentials of Co^{II}(acac)₂] and [Ni^{II}(acac)₂] are -1.95 V and -1.47 V vs. SCE, respectively, and they are more negative than that of the [Cu^{II}(acac)₂] (-0.67 V) [5]. In the case of pyrazolone complexes, the reduction potential of the three complexes ([Ni^{II}(pmbp)₂], [Co^{II}(pmbp)₂] and [Mn^{II}(pmbp)₂]) can also be predicted to be more negative than those of [Cu^{II}(pmbp)₂] and [Cd^{II}(pmbp)₂]. Therefore, the reduction peaks for Ni^{II}, Co^{II} and Mn^{II} complexes were not observed.

When the potential was scanned anodically from 0 V, a new irreversible oxidation peak appeared for all the complexes. There was no large difference among the peak potentials and they were nearly equal to each other, indicating that this peak was due to the oxidation of the pmbp ligands in the complexes.

Trivalent metal complexes. The cyclic and normal pulse voltammograms of [Fe^{III}(pmbp)₃] in CH₂Cl₂ gave a one-electron reduction peak corresponding to the reduction of [Fe^{III}(pmbp)₃] to [Fe^{II}(pmbp)₃] as shown in Fig. 3. Although the oxidation peak was observed, the oxidation process could not be discussed here because the peak overlapped with the oxidation of the background solution. The peak separation for the cathodic process at scan rate of 100 mV/s was 88 mV, indicating quasi-reversible electron transfer in CH₂Cl₂. In acetonitrile solution, however, the 70 mV peak separation indicated that the electron transfer was virtually reversible. The cyclic voltammetry of [Cr^{III}(pmbp)₃] in CH₂Cl₂ also showed only a one-electron reduction peak with 120 mV of the peak separation indicating an irreversible electron transfer process (Eq. 6).



M = Fe and Cr

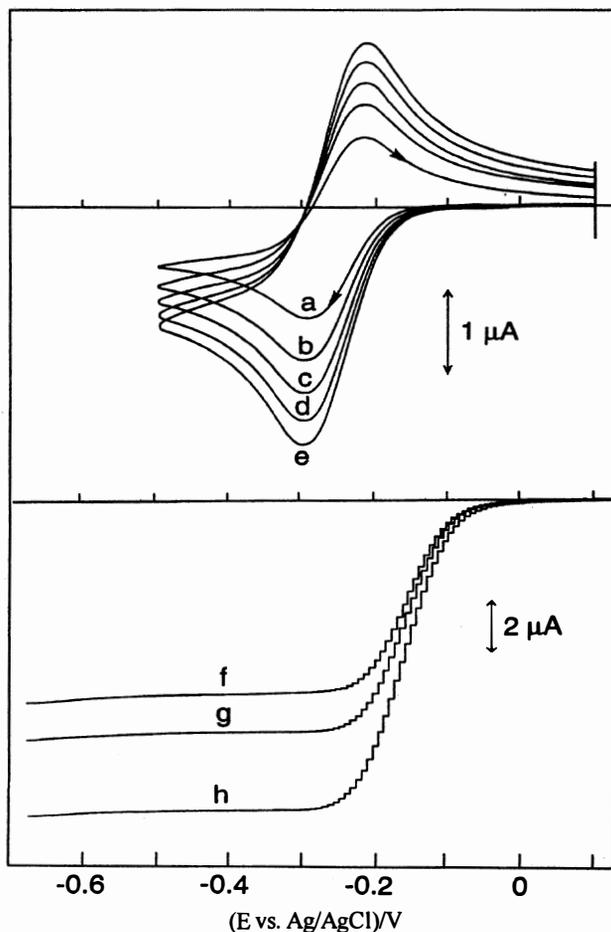


Fig 3. The cyclic (a-e) and normal pulse (f-h) voltammograms of $[\text{Fe}(\text{pmbp})_3]$ in 0.1 mol dm^{-3} TBAP-dichloromethane at 25°C . Scan rate/ mV s^{-1} : (a) 20; (b) 40; (c) 60; (d) 80; and, (e) 100. Sampling time: (f) 30 ms; (g) 50 ms, and, (h) 70 ms.

The reduction of $[\text{Fe}^{\text{III}}(\text{pmbp})_3]$ in acetonitrile solution took place at a potential value more positive than that in CH_2Cl_2 . The same results were observed in the case of tris(acetylacetonato)-iron(III) ($[\text{Fe}^{\text{III}}(\text{acac})_3]$) and tris(trifluoroacetylacetonato)iron(III) ($[\text{Fe}^{\text{III}}(\text{tfac})_3]$). This behavior might be explained by the stronger stabilization of the anionic reduced species in the solvent which has a larger dielectric constant.

The pyrazolonatoiron(III) complexes which have acyl substituents instead of benzoyl substituent, $[\text{Fe}^{\text{III}}(\text{pmC}n)_3]$ $n = 1 - 9$, also showed quasi-reversible one-electron reduction peaks in CH_2Cl_2 . The effect of the length of the alkyl chain on the reduction potential was not so large. The mid-potential, $E_{\text{mid}} [= (E_{\text{pa}} + E_{\text{pc}})/2]$ and peak separation, $\Delta E_p [= (E_{\text{pa}} - E_{\text{pc}})]$ of the trivalent metal complexes are shown in Table 3 together with $\text{p}K_a$ values of the ligands.

For many bis- and tris(β -diketonato) metal complexes, linear correlations between the redox potentials and Hammett constants of the substituent on the β -diketone or its $\text{p}K_a$ values

Table 3. Mid-potentials (E_{mid}) and peak separation (ΔE_p) of the cyclic voltammograms at scan rate = 100 mV/s of the trivalent metal complexes and $\text{p}K_a$ of the ligands.

Complex	Solvent	$E_{\text{mid}}/\text{V}^{(1)}$	$\Delta E_p/\text{mV}$	$\text{p}K_a(\text{ligand})^{(2)}$
$[\text{Fe}(\text{pmbp})_3]$	CH_2Cl_2	-0.83	88	3.80
	AN	-0.57	70	
$[\text{Fe}(\text{acac})_3]$	CH_2Cl_2	-1.24 ⁽⁴⁾		12.75 ⁽³⁾
	AN	-1.02 ⁽⁵⁾		
$[\text{Fe}(\text{tfac})_3]$	CH_2Cl_2	-0.58 ⁽⁴⁾		8.70 ⁽³⁾
	AN	-0.39 ⁽⁵⁾		
$[\text{Fe}(\text{pmC}1)_3]$	CH_2Cl_2	-0.91	106	4.17
$[\text{Fe}(\text{pmC}3)_3]$	CH_2Cl_2	-0.93	171	4.05
$[\text{Fe}(\text{pmC}4)_3]$	CH_2Cl_2	-0.94	160	4.15
$[\text{Fe}(\text{pmC}5)_3]$	CH_2Cl_2	-0.96	144	4.10
$[\text{Fe}(\text{pmC}6)_3]$	CH_2Cl_2	-0.94	157	4.10
$[\text{Fe}(\text{pmC}8)_3]$	CH_2Cl_2	-0.95	159	--
$[\text{Fe}(\text{pmC}9)_3]$	CH_2Cl_2	-0.94	134	--
$[\text{Cr}(\text{pmbp})_3]$	CH_2Cl_2	-0.98	120	3.80
$[\text{Cr}(\text{acac})_3]$	AN	-2.03 ⁽⁶⁾		12.75 ⁽³⁾
$[\text{Cr}(\text{fhfa})_3]$	AN	-0.26 ⁽⁶⁾		6.0 ⁽³⁾

(1) vs. Fc^+/Fc ; (2) in 10% dioxane- H_2O , 25°C ; (3) in 75% dioxane- H_2O , 30°C ; (4) McCarthy, H. J. and Tocher D. A., *Polyhedron*, 6, 1421 (1987); (5) Sock, O. et al., *Electrochim. Acta*, 26, 99 (1981); and, (6) Gritzner, G. et al. *Electroanal. Chem.* 101, 177 (1979).

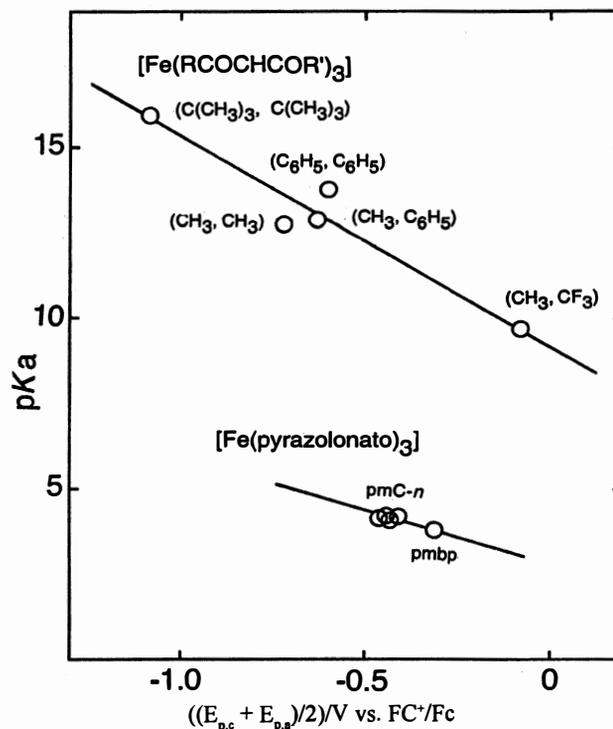


Fig. 4. The relationship between the mid-potentials of $[\text{Fe}(\beta\text{-diketonato})_3]$ and $[\text{Fe}(\text{pyrazolonato})_3]$ and $\text{p}K_a$ values of the ligands.

are well known [3, 6–9]. Linear correlation was also observed for the reduction potentials of tris(β -diketonato) iron(III) complexes in CH_2Cl_2 [6]. The plots of $\text{p}K_a$ values of β -diketone against the reduction potential of tris(β -diketonato)iron(III) are shown in Fig. 4 together with those for pyrazolonatoiron(III) complexes. A linear relationship was also established for pyrazolonato-iron(III) complexes. However, the straight line for the pyrazolonato complexes was below that of β -diketonato complexes, and the slopes of the lines were slightly different. This might be caused by the difference in the substituent effects on $\text{p}K_a$ values between the β -diketone and pyrazolone. The pyrazolone has a β -diketonato ring but it joins a pyrazolone ring directly. The pyrazolone ring should affect strongly the $\text{p}K_a$ value and the reduction potential of its iron(III) complex.

CONCLUSION

This study has elucidated the electrochemical behavior of the metal complexes of 1-phenyl-3-methyl-4-benzoyl-5-pyrazolone and its acyl derivatives. The lanthanide and divalent complexes exhibited similarity in their electrochemical properties. The ligand is involved in their oxidation. Linear correlation between the reduction potentials of the pyrazolonatoiron(III) complexes and the $\text{p}K_a$ value of the ligands was also established. This was found to be different from that of the β -diketonato complexes mainly due to substituent effects. The same trend may be applicable to the chromium(III) complexes.

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