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Research Article

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Synthesis and dye degradation properties of Cu^{2+} complexes with pyrazole derivatives

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ABSTRACT

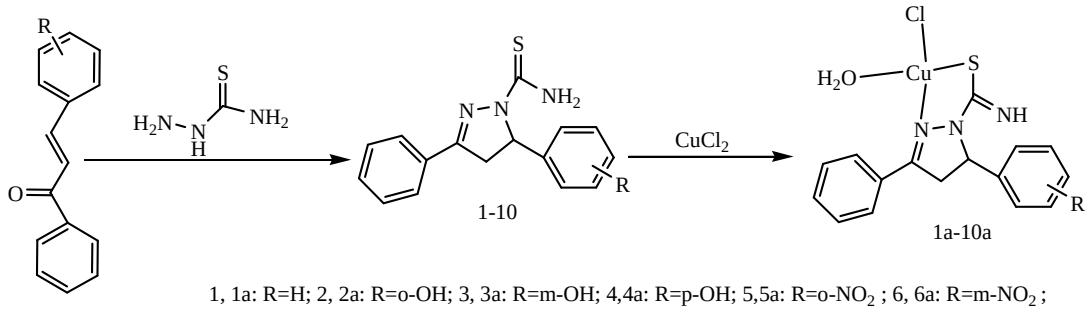
Ten pyrazole derivatives were synthesized and characterized by IR spectra, 1H-NMR spectra and MS spectra. The coordination reaction of the derivatives with $CuCl_2$. And ten novel Cu(Ⅱ) complexes with the derivatives were prepared and characterized by IR spectra and elemental analysis. The catalytic degradation of methyl orange aqueous solution was investigated using the complexes as catalysis in presence H_2O_2 by HPLC method and Vis-spectrophotometry. The result of characterization showed that there are four coordination sites around Cu(Ⅱ) in all complexes, which are respectively occupied by one sulfur atom (from the derivative), one nitrogen atom(from the derivative), one oxygen atom(from the H_2O) and one chloro atom(from the Cl^-). The degradation of methyl orange indicated that all the complexes show the properties of enzyme activity. And the main degradation product determined was maleic acid. And the mechanism of the catalysis was deduced.

Keywords: Pyrazole, Complex, Synthesis, catalysis, degradation of methyl orange.

INTRODUCTION

In serious consideration of the worldwide environmental issues associated with the extensive use of the textile dyes and effluents generated thereof[1,2], the scientists across the world are in search for potential treatment technologies for their treatment. The existing physical/chemical technologies that are usually expensive and commercially or environmentally unattractive[3,4]. Biological processes seem as potential alternatives because they are cost effective, eco-friendly and can be applied to wide range of dye containing industrial effluents[5,6,7,8]. Over the last few decades, intensive research in the area of enzyme technology has provided many approaches that facilitate their practical applications. Among them, the newer technological developments cannot offer the possibility of a wider and more economical exploitation of biocatalysts in industry, waste treatment[9]. Decolorization of dye wastewater by some oxidase is the subject of many studies. Laccase is the most important with potentially advantageous containing copper[10]. However, their high production cost, low operational stabilities, availability in small amounts, susceptibility to attack by proteases and activity inhibition limit their commercial applications in industrial and environmental biotechnology. Therefore, innovative treatment technologies need to be investigated. Artificial enzyme was a new type of catalyst developed and researched[11,12], which overcame the shortcomings such as the traditional heat-sensitive, poor stability, the limited sources, as well as the limitations of the conditions. Complexes could be used as the modelenzyme of the active part of metal enzyme.

In order to obtain the modelenzyme of the laccase to treat the dye wastewater, and search for a novel technologies for dye degradation. Ten pyrazole derivatives and their complexes with $CuCl_2$ were prepared(Scheme 1) and characterized. And herein the catalytic properties of the complexes in the degradation of methyl orange were reported. And the mechanism of the catalysis was deduced. The complexes of copper are therefore most useful.



1, 1a: R=H; 2, 2a: R=o-OH; 3, 3a: R=m-OH; 4,4a: R=p-OH; 5,5a: R=o-NO_2 ; 6, 6a: R=m-NO_2 ;

7,7a: R=p-NO_2; 8,8a: R=p-CH_3 ; 9, 9a: R=p-Cl , 10,10a: m-R=NH_2

Scheme 1 the synthesis of the ligand and the complexes

EXPERIMENTAL SECTION

The chalcone derivatives were synthesized according to a literature procedure[13]. All the other reagents were commercially available and used without further purification.

IR spectra were measured on an FI-IR-170 (Nicolex) spectrometer with KBr pellets. ^{13}CNMR-spectra were run on a Bruker 400 Ultra Shield^{TM} (400MHz) spectrometer using TMS as internal standard and $CDCl_3$ as the solvent. The mass spectra were obtained on a Saturn 2200 spectrometer. Absorbance spectra were recorded using a spectrophotometer (Agilent 7530G). The melt point was determined on a XT-1 apparatus uncorrected. The Cu contents in complexes were determined by EDTA complexometric titration.

1 Synthesis of the compounds 1-10

The corresponding chalcone derivative (5mmol), thiosemicarbazide (10mmol, 0.91g) and alcohol(20mL) were added to a flask and stirred at the temperature. Then the alcohol solution of potassium hydroxide(0.3g, 10mL) was added to the above mixture. Then the mixture was heated to reflux and stirred for 5h while refluxing. The mixture was cooled gradually to the room temperature and stirred for another 12h.The solid was filtered and washed three times with ice water to give the rude product. The solid was recrystallized from ethanol to give the compound 1-10.

2-phenyl-5-phenyl-pyrazole-1-thioformamides (1): Pale yellow. Yield 64%. M.P. 200~202℃. IR (KBr pellet, cm^{-1}): 3483, 3349（ν_{N-H}）,1573, 1500, 1472, 1443, 1417, 1363, 1342, 1266, 1070. ^{1}H-NMR（400MHz, $CDCl_3$）δ: 7.73(d, 2H), 7.10-7.46(m, 9H), 6.15(s,1H), 6.06(dd, 1H), 3.88(dd, 1H), 3.23(dd,1H).

2-phenyl-5-o-hydroxyl-phenyl-pyrazole-1-thioformamides (2): White. Yield 70%. M.P. 245～247℃. IR(KBr pellet, cm^{-1}): 3443, 3319, 3171, 1615, 1603, 1538, 1490, 1463, 1367, 1266, 1201, 1149, 1111, 1061. ^{1}H-NMR(400MHz, $CDCl_3$) δ: 8.36~6.72 (m, 14H), 2.5(s, 1H).

2-phenyl-5-m-hydroxyl-phenyl-pyrazole-1-thioformamides (3): Pale white. Yield 55%. M.P. 251～253℃.IR(KBr pellet, cm^{-1}): 3431, 3328, 3251, 3143, 1588,1568, 1488, 1448, 1421, 1376, 1342, 1210, 1142, 1091. ^{1}H-NMR(400MHz, $CDCl_3$) δ: 8.36~7.02 (m, 14H), 2.97(s, 1H).

2-phenyl-5-p-hydroxyl-phenyl-pyrazole-1-thioformamides (4): Pale yellow. Yield 65%. M.P. 247～249℃. IR(KBr pellet, cm^{-1}): 3443, 3319, 3174, 1615, 1604, 1538, 1490, 1464, 1367, 1266, 1202, 1062. ^{1}HNMR(400MHz, $CDCl_3$) δ: 8.27~7.03 (m, 14H), 2.72(s, 1H).

2-phenyl-5-o-nitro-phenyl-pyrazole-1-thioformamides (5): Brown. Yield. 68 %. M.P. 262~264℃. IR(KBr pellet, cm^{-1}):3472, 3387, 3246, 1670, 1604, 1512, 1462, 1446, 1341, 1290, 1216, 1074, 1012. ^{1}HNMR(400MHz, $CDCl_3$) δ: 8.17~ 8.12(m, 2H), 7.75~7.70 (d, 2H), 7.60~7.35 (m, 6H), 3.95 (dd, 1H), 3.20 (dd, 1H).

2-phenyl-5-m-nitro-phenyl-pyrazole-1-thioformamides (6): Brown. Yield 48%. M.P. 268～271℃. IR(KBr pellet, cm^{-1}): 3431, 3351, 1581, 1528, 1468, 1445, 1345, 1094. ^{1}H NMR(400MHz, $CDCl_3$) δ: 8.17~8.12 (m, 2H), 7.75~7.70 (d, 2H), 7.60~7.35 (m, 6H), 3.95 (dd, 1H), 3.20 (dd, 1H).

2-phenyl-5-p-nitro-phenyl-pyrazole-1-thioformamides (7): Brown. Yield 63 %. M.P. 264～267℃. IR(KBr pellet, cm^{-1}): 3431, 3365, 1582, 1513, 1464, 1445, 1344, 1282, 1179, 1092, 1013. ^{1}H NMR(400MHz, $CDCl_3$) δ: 8.17~8.12 (m, 2H), 7.75~7.70 (d, 2H), 7.60~7.35 (m, 6H), 3.95 (dd, 1H), 3.20 (dd, 1H).

2-phenyl-5-p-methyl-phenyl-pyrazole-1-thioformamides (8): Pale white. Yield 71 %. M.P. 172～174℃. IR(KBr pellet, cm^{-1}): 3393, 3270, 3155, 1614, 1587, 1512, 1465, 1376, 1089. ^1H NMR(400MHz, $CDCl_3$) δ: 7.75~7.05 (m, 10H), 6.02 (dd, 1H), 3.90~3.65 (m, 2H), 3.20 (dd, 1H), 2.30 (s, 3H).

2-phenyl-5-p-chloro-phenyl-pyrazole-1-thioformamides (9): Pale white. Yield 62 %. M.P. 164～165℃. IR(KBr pellet, cm^{-1}): 3389, 3270, 3154, 1614, 1578, 1471, 1445, 1376, 1348, 1089, 1013. ^1H NMR(400MHz, $CDCl_3$) δ: 7.75~7.10 (m, 10H), 6.02 (dd, 1H), 3.85 (dd, 1H), 3.72(dd, 1H), 3.20 (dd, 1H).

2-phenyl-5-m-amino-phenyl-pyrazole-1-thioformamides (10): Yellow. Yield 53 %. M.P. 178～181℃. IR(KBr pellet, cm^{-1}): 3389, 1676, 1597, 1492, 1447, 1026. ^1H NMR(400MHz, $CDCl_3$) δ: 8.15~7.35 (m, 10H), 6.15 (dd, 1H), 3.95 (dd, 1H), 3.74 (dd, 2H), 3.22 (dd, 2H).

2 Synthesis of the complexes 1a-10a

A solution of 0.80g $CuCl_2$ (6mmol) in 40mL of 95% alcohol was added into a solution of the ligand (5 mmol) in 60mLof 95% alcohol at 80°C. And the mixture was stirred for 4h. Then the solid was filtered and washed. The complexes 1a-10a were obtained.

3 Investigation of methyl orange degradation of the complexes 1a-10a

The complex (0.001mmol) and H_2O_2 (1.0mL, 30%, 10mmol) were added into the methyl orange solution(15mg/L, 500mL, 0.02mmol) and stirred at room temperature. The A (absorbance) of the mixture was determined by Vis-spectra(λ=470nm) method. The declorization rate of methyl orange to time curve was plotted. The declorization rate of methyl orange was calculated as following.

$Rate(\%) = \frac{A_0 - A_t}{A_0} \times 100\%$ (A_0 is the value at t=0 min, A_t is the value at t min.)

The products of the degradation were determined by RP-HPLC-DAD method. The separation was carried out on a ODS C18 column(150mm×4.6mm) at room temperature. The column, stainless steel packed with Wondasil, 5um C18. Mobil phase was 20% H_2O in methanol(V/V). Detector is DAD at λ=220nm.

The blank experiment was done in absence of any complexes as the above.

RESULTS AND DICUSSION

Composition and structure of the complexes were determined by the IR spectra and elemental analysis. The results were listed in Table 1.

Table 1 Composition and structure of the complexes

Complex	Elemental analysis, % Found (calculate)				IR spectra (cm^{-1})	
	C	H	N	M	ligand	complex
1a $C_{16}H_{16}N_3SOCuCl$	48.72 (48.35)	4.17 (4.07)	10.79 (10.58)	15.13 (15.99)	3483, 3349, 1573, 1500, 1472, 1443	3433, 1585, 1532, 1497,1423
2a $C_{16}H_{16}N_3SO_2CuCl$	46.84 (46.48)	4.09 (3.93)	10.23 (10.17)	15.65 (15.38)	3443, 3319, 3173, 1615, 1603, 1538, 1490, 1463	3378, 1604, 1578, 1487, 1443
3a $C_{16}H_{16}N_3SO_2CuCl$	46.19 (46.48)	3.89 (3.93)	10.32 (10.17)	14.78 (15.38)	3431, 3328, 3143, 1588, 1568, 1488, 1448, 1421	3426, 1590, 1532, 1492, 1446
4a $C_{16}H_{16}N_3SO_2CuCl$	46.28 (46.48)	4.21 (3.93)	10.40 (10.17)	14.72 (15.38)	3443, 3319, 3174, 1615, 1604, 1538, 1490, 1464	3427, 1605, 1573, 1538, 1443
5a $C_{16}H_{15}N_4SO_3CuCl$	43.13 (43.43)	3.58 (3.42)	12.70 (12.67)	13.87 (14.37)	3472, 3387, 3246, 1670, 1604, 1512, 1462, 1446	3267, 1613, 1522, 1482, 1462
6a $C_{16}H_{15}N_4SO_3CuCl$	43.57 (43.43)	3.24 (3.42)	12.82 (12.67)	13.92 (14.37)	3431, 3351, 1581, 1528, 1468, 1445	3447, 1570, 1529, 1490, 1458
7a $C_{16}H_{15}N_4SO_3CuCl$	43.08 (43.43)	3.82 (3.42)	12.69 (12.67)	13.79 (14.37)	3431, 3365, 1582, 1513, 1464, 1445	3447, 1660, 1631, 1607, 1457
8a $C_{17}H_{18}N_3SOCuCl$	50.57 (49.62)	4.32 (4.42)	10.12 (10.22)	14.93 (15.45)	3393, 3270, 3155, 1614, 1578, 1512, 1465	3421, 3254, 1587, 1532, 1493, 1446, 1424
9a $C_{16}H_{15}N_3SOCuCl_2$	44.37 (44.50)	3.85 (3.58)	10.02 (9.73)	14.19 (14.71)	3389, 3270, 3154, 1614, 1578, 1471, 1445	3429, 3254, 1590, 1567, 1528, 1492, 1446
10a $C_{16}H_{17}N_4SOCuCl$	46.17 (46.59)	4.38 (4.16)	13.67 (13.59)	14.89 (15.41)	3389, 1597, 1552, 1492, 1447	3230, 1529, 1446

Data in Table 1 indicated that the composition deduced by calculation agrees well with the experimental data. The IR spectra of all the complexes shows the broad absorption bands at 3300~3500 cm^{-1} region resulting from stretching vibrations of O-H in molecule H_2O. The IR spectra of all the complexes shows absorption bands resulting

from the skeletal vibrations of the Ar-cycle at 1400~1600cm^{-1}, which is difference from the absorption of the corresponding ligand. Compared with the corresponding ligand, the absorption bands of the complex at 3200~3350cm^{-1} were resulted from the skeletal vibrations of the =N-H, but the absorption bands of the corresponding ligand at 3200~3350cm^{-1} were resulted from the skeletal vibrations of the H-N-H. All these indicated one oxygen atom from H_2O, one chloride, one nitrogen atom and sulfur atom from the ligand close to Cu^{2+} coordination.

The A (absorbance) of the mixture was determined by Vis-spectra(λ=470nm) method. The results were showed in Fig.1.

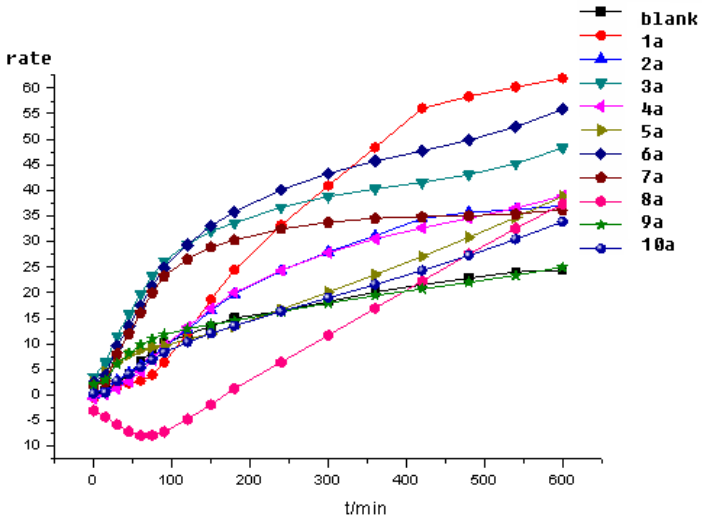


Fig.1 The declorization rate of methyl orange to time curve

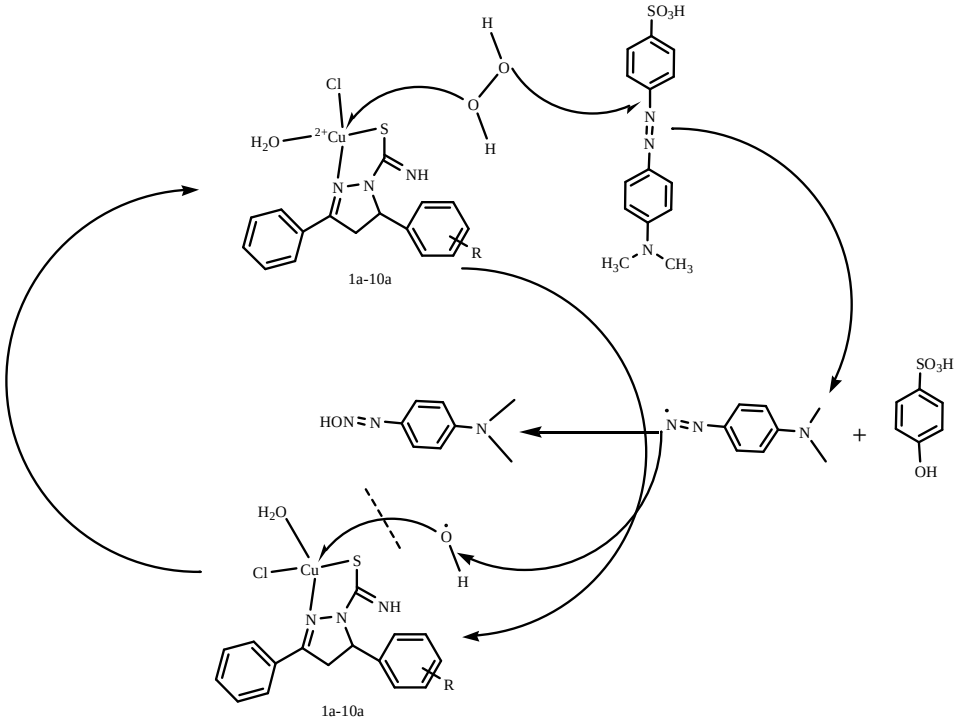


Fig.2 the catalysis mechanism of the complex

The linear regression equation have been obtained by using the least-squares method. The results was listed in Table 2.

Table 2 the linear regression equation

	Linear1(k_1)	Linear 2(k_2)	k_2/k_1
blank	Y=0.0425x-0.9902		------
1a	Y =-0.2603+0.0565X	Y =-5.337+0.1512X	2.68
2a	Y =0.0228+0.0982X	Y =-1.133+0.1166X	1.19
3a	Y =3.630+0.1873X	Y =3.435+0.2620X	1.40
4a	Y =-0.7057+0.0636X	Y =-3.352+0.1375X	2.16
5a	Y=8.014+0.0187X	Y =3.102+0.0583X	3.12
6a	Y=2.618+0.0871X	Y=1.994+0.2563X	2.94
7a	Y=1.892+0.0486X	Y=1.242+0.2455X	5.05
8a	Y=-7.892+0.006X	Y=-14.74+0.0877X	14.62
9a	Y=2.01+0.0667X	Y=3.037+0.1095X	1.64
10a	Y=0.35+0.0101X	Y=0.7232+0.0791X	7.83

Data in Fig.1 and Table 2 show that all the complexes show catalytic activity of enzyme in the degradation of methyl orange. There exist postponing stage and linear increasing stage. The complexes 2a is the worst, and the complex 8a is the best. The catalysis mechanism of biomimetric catalysis, the prepared complexes, which were used as catalysis in the reaction of the methyl orange degradation, was deduced (Fig.2).

The products of the degradation were determined by RP-HPLC-DAD method. The results show that the products were phenol, hydroquinone and maleic acid.

Acknowledgements
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