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Synthesis of Azo-conjugated Catecholate Complexes and their Photo- and Proton-responses

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Summary: A new azo-conjugated catecholate ligand, **azocat**, and its nickel complexes were synthesized, and their physical and chemical properties were investigated. The complex with one **azocat** shows no obvious photo-response, whereas the compound with two **azocat**'s causes a little photoisomerization. Both of these novel azo-conjugated catecholate complexes show remarkable proton responses.

Keywords: charge transfer; crystal structures; electrochemistry; isomerization; photochemistry

Introduction

A molecule comprising multiple functional moieties, connected via a π-conjugated chain, can afford unique properties based on the electronic inter-moiety interaction. Azo-conjugated transition metal complexes are involved in such multi-functional molecules, because the azo group undergoes reversible photoisomerization and the metal complexes exhibit unique electronic, optical and magnetic properties. In the previous study, we have synthesized novel azo-conjugated metalladithiolenes, and have found the curious proton and photo response for dppe-M (dppe = 1,2-diphenylphosphinoethane, M = Ni, Pd, Pt) complexes (Scheme 1).[1,2] Dioxolene is a unique ligand that can take a number of electronic states due to the combined electrochemical activity of the metal ion and the quinone ligands.[3-6] In this paper, we describe the synthesis of a new azo-catecholate ligand, **azocat**, and two complexes, an mono-**azocat** Ni (II) complex with dppe as a co-ligand, and a bis-**azocat** Ni (II) complex. We also present the proton- and photo-response of these complexes.

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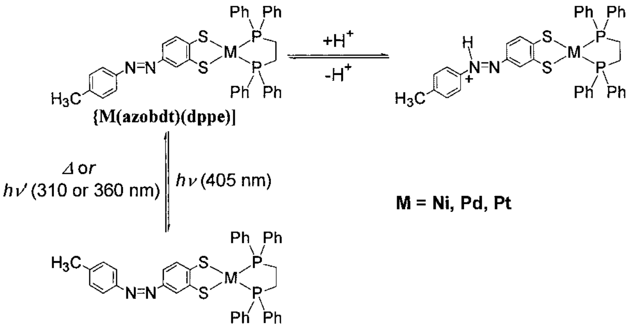
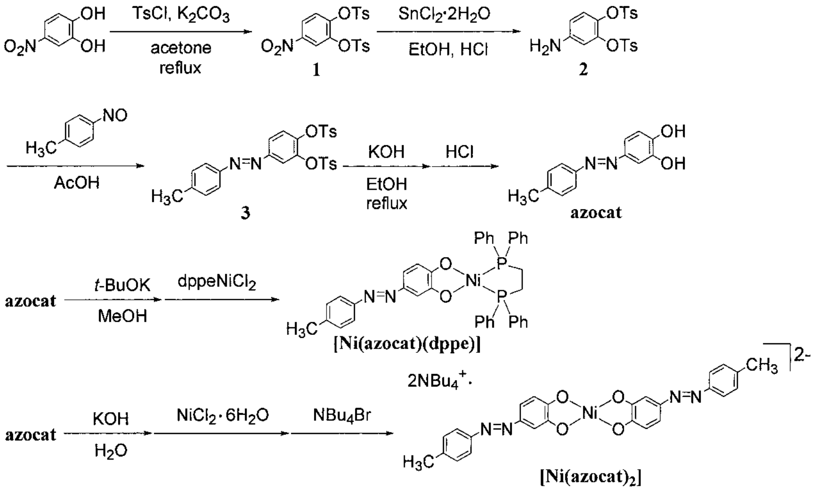


Scheme 1.

Experimental Section

Synthesis



Scheme 2.

4-Nitro-1’, 2’-bis (toluenesulfonyl) catechol, 1

p-Toluenesulfonyl chloride was slowly added to a mixture of 4-nitrocatechol (5.00 g, 0.0322 mol) and potassium carbonate (9.80 g, 0.0709 mol) in acetone (300 ml) over 1 h. After the solution was refluxed for 2.5 h and evaporated, the solid was dissolved with ethyl acetate and washed with water. The organic solution was evaporated, and the product was recrystallized from methanol to yield 14.0 g (0.0303 mol, 93.9%) of **1**. ^{1}H NMR (270 MHz, $CDCl_3$) δ 8.15 (dd, *J* = 9.2, 2.7 Hz 1H, Ph), 8.09 (d, *J* = 2.7 Hz 1H, Ph), 7.67 (d, *J* = 8.1 Hz 4H, Ts), 7.50 (d, *J* = 9.2 Hz 1H, Ph), 7.32 (d, *J* = 8.1 Hz 4H, Ts), 2.48 (s, 3H, Ts), 2.47 (s, 3H, Ts). Anal. Calcd for $C_{20}H_{17}N_2O_8S_2$: C, 51.83%; H, 3.70%; N, 3.02%. Found: C, 51.68%; H, 3.68%; N, 3.08%.

4-Amino-1', 2'-bis (toluenesulfonyl) catechol, 2

The ethanol solution (26 ml) of $SnCl{\cdot}6H_2O$ (14.5 g, 0.0643 mol) was added to the stirred solution of **1** (9.87 g, 0.0213 mol) in hydrochloric acid 26 ml and ethanol 13 ml, and then refluxed for 12 h. The solution was added to a stirred solution of $SnCl{\cdot}6H_2O$ (14.5 g, 0.0643 mol) in hydrochloric acid 9 ml and ethanol 13 ml, and then refluxed for 3 h. After cooling, the solution was neutralized by NaOH and washed with ethyl acetate. The organic solution was evaporated, and the product was recrystallized from ethanol to yield 7.98 g (0.0184 mol, 86.4%) of **2**. ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.65 (d, *J* = 8.4 Hz 2H, Ts), 7.58 (d, *J* = 8.4 Hz 2H, Ts), 7.27 (d, *J* = 8.4 Hz 2H, Ts), 7.24 (d, *J* = 8.4 Hz 2H, Ts), 6.96 (d, *J* = 8.4 Hz 1H, Ph), 6.56 (d, *J* = 2.7 Hz 1H, Ph), 6.45 (dd, *J* = 8.4, 2.7 Hz 1H, Ph), 3.79 (s, 2H, NH_2), 2.45 (s, 3H, Ts), 2.44 (s, 3H, Ts). Anal. Calcd for $C_{20}H_{19}NO_6S_2$: C, 55.42%; H, 4.42%; N, 3.23%. Found: C, 55.23%; H, 4.36%; N, 3.28%.

4'-Tolylazobenzo-1, 2-bis (toluenesulfonyl) catechol, 3

The mixture of **2** (2.69 g, 6.22 mmol) and 4-nitrosotoluene (0.754 g, 6.22 mmol) in acetic acid 60 ml was refluxed for 3 h. The solution was evaporated and purified by silica-gel column chromatography with chloroform as an eluent. The orange-band component was evaporated to yield 1.66 g (3.10 mmol, 49.8%) of **3** ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.81-7.77 (m, 4H, Ph, Tol), 7.66 (d, *J* = 8.4 Hz 2H, Ts), 7.62 (d, *J* = 8.4 Hz 2H, Ts), 7.39 (dd, *J* = 7.6, 2.2 Hz 1H, Ph), 7.32-7.26 (m, 6H, Tol, Ts), 2.44 (s, 3H, Me), 2.43 (s, 6H, Ts, Me). Anal. Calcd for $C_{27}H_{24}N_2O_6S_2$: C, 60.43%; H, 4.51%; N, 5.22%; S, 11.95%. Found: C, 60.40%; H, 4.51%; N, 5.22%; S, 11.92%.

4'-Tolyl-4-azobenzocatechol, azocat

All manipulations were carried out under nitrogen. KOH (1.08 g, 0.0192 mol) was added to the stirred solution of **3** (500 mg, 0.932 mmol) in ethanol (30 ml) and refluxed for 1.5 h. After cooling, the solution was neutralized by HCl aq (15 ml, 0.960 mol/l). The resulting precipitate was filtered and washed with water to yield 298 mg (89.9%) of the mixture of **azocat** and *p*-toluenesulfonic acid. Their mole ratio was evaluated at 5:3 based on the ^{1}H NMR spectrum. The ^{1}H NMR signals ascribed to **azocat** are as follows; ^{1}H NMR (270 MHz, acetone-d_6) δ 8.63 (s, 1H, OH), 8.39 (s, 1H, OH), 7.74 (d, J = 8.4 Hz 2H, Tol), 7.45 (d, J = 2.2 Hz 1H, Ph), 7.41 (dd, J = 8.4, 2.2 Hz 1H, Ph), 7.33 (d, J = 8.4 Hz 2H, Tol), 7.00 (d, J = 8.4 Hz 1H, Ph), 2.40 (s, 3H, Me).

[1,2-Bis(diphenylphosphino-κ*P*)ethane]{4-[(4-methylphenyl)-azo]-1,2-catecholato-κ*S*, κ*S*'}-nickel(II), [Ni(azocat)(dppe)]

All manipulations were carried out under nitrogen. *t*-BuOK (40.0 mg, 0.356 mmol) was added to the stirred solution of the mixture of **azocat** and *p*-toluenesulfonic acid (51.7 mg) in methanol (20 ml) and stirred for 20 min. dppeNiCl$_2$ (159 mg, 0.30 mmol) was then added to the solution and stirred further for 48 h at r.t. The resulting precipitate was filtered and washed with methanol to yield 49.7 mg (0.073 mmol, 46.6%) of **[Ni(azocat)(dppe)]** as red-brown powder. ^{1}H NMR (270 MHz, CDCl$_3$) δ 8.25-8.00 (m, 8H, dppe), 7.65 (d, J = 8.4 Hz 2H, Tol), 7.60-7.44 (m, 12H, dppe), 7.23 (d, J = 8.4 Hz 2H, Tol), 7.13-7.07 (m, 2H, Ph), 6.61 (d, J = 8.4 Hz 1H, Ph), 2.38 (s, 3H, Me), 2.33 (d, J = 8.1 Hz 4H, dppe); IR (KBr pellet) ν 1475(s), 1435(s), 1281(s). Anal. Calcd for $C_{39}H_{34}N_2O_2S_2 \cdot 0.25H_2O$: C, 68.10%; H, 5.06%; N, 4.07%. Found: C, 68.11%; H, 5.03%; N, 4.10%.

Tetrabutylammonium bis{4-[(4-metylphenyl)azo]-1,2-catecholato-κ*S*, κ*S*'}nickel(II), [Ni(azocat)$_2$]

All manipulations were carried out under nitrogen. KOH (56.1 mg, 1.00 mmol) was added to the stirred solution of the mixture of **azocat** and *p*-toluenesulfonic acid (114 mg) in water (30 ml) and stirred for 30 min. NiCl$_2$·6H$_2$O (59.2 mg, 0.250 mmol) was then added to the solution. After 3h, Bu$_4$NBr (161 mg, 0.500 mmol) *aq*. was added to the deep red solution and filtered and washed with water to yield 105 mg (0.105 mmol, 61.2 %) as red powder. The powder was recrystallized from dichloromethane/diethylether to yield fine red crystals. ^{1}H NMR (500MHz, CD_2Cl_2) δ7.45 (d, J = 8.1 Hz 4H, Tol), 7.18 (d, J = 8.1 Hz 4H, Tol), 6.89 (d, J = 8.1 Hz 2H, Ph), 6.19 (m, 2H, Ph), 5.82 (d, J = 8.1 Hz 2H, Ph), 3.76-3.25 (m, 16H, Bu), 2.39 (s, 6H, Me), 1.96-0.88 (m, 56H, Bu); IR (KBr pellet) ν2962(m), 2875(m), 1477(m), 1277(s).

X-ray Crystallography

A crystal obtained by recrystallization from dichloromethane/diethyl ether was mounted on a glass loop fiber with liquid paraffin and liquid paraffin was frozen in the cold stream, and data was collected at 113 ± 1 K (Rigaku Mercury diffractometer coupled with a CCD area detector with graphite monochromated Mo-Kα radiation (0.7107 Å)). The data were collected to a maximum 2θ value of 55.0° and the detector swing angle was 20°. A sweep of data was done using ϕ scans from -80.0 to 100.0° in 0.3° step, at ω = 0.0° and χ = 0.0°. A second sweep was performed using ω scans from -20.0 to 28.0° in 0.3° step, at χ = 90.0° and ϕ = 0.0°. Another sweep was performed using ω scans from -20.0 to 28.0° in 0.3° step, at χ = 90.0° and ϕ = 90.0°. Another sweep was performed using ω scans from -20.0 to 28.0° in 0.3° step, at χ = 90.0° and ϕ = 180.0°. Another sweep was performed using ω scans from -20.0 to 28.0° in 0.3° step, at χ = 90.0° and ϕ = 270.0°. An emorical absorption correction was applied. The structure was solved by direct methods and expanded using Fourier techniques. Hydrogen atoms were not included in the calculations. All calculations were performed using the CrystalStructure crystallographic software package of the Rigaku Co. and the Molecular Structure Co.

Results and Discussion

Synthesis

Amino compound **2** derived from nitro compound **1** is a catecholate-protected compound, which can react with a number of organic and other functional molecules containing nitroso groups to afford various symmetric and asymmetric azo-conjugated catecholate complexes. This protecting group can be cleaved by treating either in basic media or with nucleophilic reagents, whereas it is stable in strong acidic media and is resistant to strong reduction and mild oxidation. Thus, this group is one of the most suitable protecting groups for the construction of the azo group by reduction and oxidation in acidic media.

X-ray Crystallographic Analysis

A single crystal suitable for X-ray crystallographic analysis was obtained for **[Ni(azocat)$_2$]** by recrystallization from dichloromethane/diethylether. An ORTEP diagram for **[Ni(azocat)$_2$]** is displayed in Figure 1. The configuration around the metal center is a typical tetra-coordinated square-planar structure. The dioxolene ring was a planar five-membered ring. The bond lengths of Ni-O1 and Ni-O2 were 1.868(9) and 1.861(8) Å within the usual range of Ni-O distances for other square-planar dioxolene complexes.[7,8] **[Ni(azocat)$_2$]** has a nearly planar azobenzene structure that is coplanar with the dioxolene ring, as can be seen in the angle between the azobenzene structure and the dioxolene moiety of 16.04°. The N1-N2 bond length in **[Ni(azocat)$_2$]** was 1.281(7) Å which lies in the normal range of 1.23-1.27 Å for organic azobenzenes.[9,10]

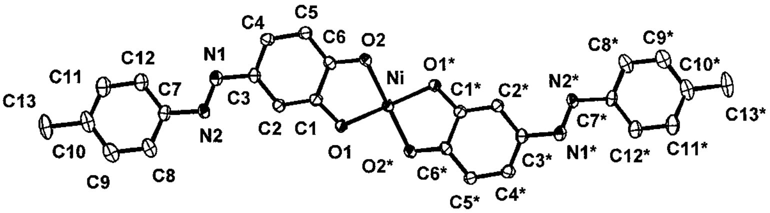


Fig. 1. ORTEP drawing of **[Ni(azocat)$_2$]** omitted tetrabutylammonium with 50% probability of ellipsoids.

Photo Response

UV-vis absorption spectra of **[Ni(azocat)(dppe)]** and **[Ni(azocat)$_2$]** in dichloromethane were shown in Figure 2. A strong absorption appears at 465 nm for the former and 534 nm for the latter. Photoirradiation was carried out for **[Ni(azocat)(dppe)]** and **[Ni(azocat)$_2$]**. The molar ratio of the cis-form reached in the photostationary state (PSS) is shown in Table 1. While an azo-conjugated metalladithiolene of Ni(II) with diphenylphosphinoethane as a co-ligand, **[Ni(azobdt)(dppe)]**, showed a photo-response by irradiation, **[Ni(azocat)(dppe)]** did not show an obvious photo response. The absence of trans-cis photoisomerization might be due to the contribution of the energy-transfer pathway at the complex, as there is a strong absorption at the visible region. **[Ni(azocat)$_2$]** showed a little photo-response. The reason for the low molar ratio of **[Ni(azocat)$_2$]** is a weak absoption at the visible region, which is also seen in the case of **[Ni(azocat)(dppe)]**.

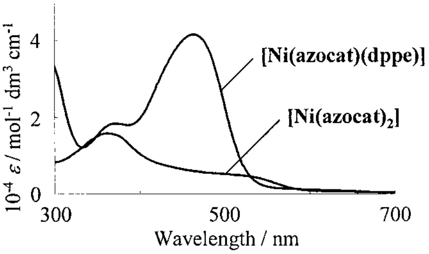


Fig. 2. UV-vis spectra of **[Ni(azocat)(dppe)]** and **[Ni(azocat)$_2$]** in CH_2Cl_2.

Table 1. Spectral Data and Cis Molar Ratios in the Photostationary State of the Complexes.

Complex	λ_{max} / nm [a] ($10^{-4}\varepsilon$ / mol^{-1} dm^{-3} cm^{-1})	θ_{cis} / %
[Ni(azobdt)(dppe)] [b]	418 (1.82)	42 [e]
[Ni(azocat)(dppe)] [c]	465 (4.15)	not observed
[Ni(azocat)$_2$] [c]	534 (0.44) (sh) [d]	5 [f]

a) Wavelength and molar extinction coeffcient at the absorption maximum of the band. b) In acetonitrile. c) In dichloromethane. d) A shoulder peak. e) Cis molar ratio at excitation at 405 nm in the photostationary state. f) Cis molar ratio at excitation at 366 nm in the photostationary state.

Proton Response

A compound **[Ni(azocat)(dppe)]** exhibited unusual proton response together with a drastic change in color. Figure 3 shows the spectral changes in **[Ni(azocat)(dppe)]** upon addition of trifluoromethanesulfonic acid. The spectral change of **[Ni(azocat)(dppe)]** occurs in two steps with showing the isosbestic point on addition of the acid between 0.0-1.0 eq. and 1.5-3.0 eq., respectively, indicating that two types of protonation to the complex take place. With an increase in the amount of the acid between 0.0-1.0 eq., the band at 465 nm decreases in intensity, and a new strong band appears in the visible region. The color was changed from yellow to red-purple. Reverse spectral changes were achieved with the addition of potassium *tert*-butoxide. This spectral behavior is similar to that of the azo-conjugated metalladithiolenes, thus indicating that protonation of the azo moiety had taken place (Figure 3 (c)). To examine the proton response further, an electrochemical measurement was carried out upon addition of the acid to **[Ni(azocat)(dppe)]**. Upon addition of the acid, a new wave was observed at −0.66 V vs Ag/Ag$^+$. The finding clearly demonstrates that the protonation of the azo moiety induces a significantly positive shift of the reduction potential of the azo moiety. The single protonation is supported by the result of the ESI-mass spectroscopic measurement, which show a peak at *m/z* 683.2 in the complex, and with clearly isotope pattern of **[Ni(azocat)(dppe)]**-H$^+$. The protonation to the nitrogen atom bound to the tolyl moiety reasonably afforded the conjugated structure that delocalized the charge beyond the dioxolene moiety. The dioxolene moiety, which was strongly conjugated with the azo group, increased the basicity of the azo group with a resonance stabilization effect, which in turn led to the observed facilitated protonation behavior.

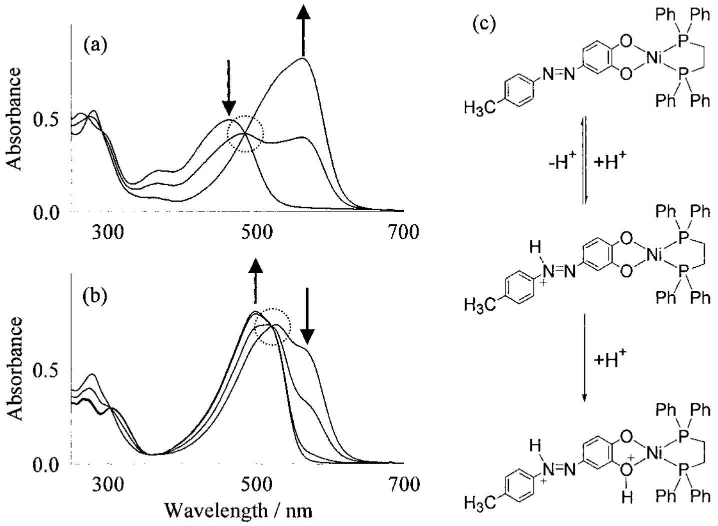


Fig. 3. UV-vis spectral changes of **[Ni(azocat)(dppe)]** in CH_2Cl_2 upon addition of 0.0-1.0 eq. (a) and 1.5-3.0 eq. (b) of CF_3SO_3H (c) The protonation pathway of **[Ni(azocat)(dppe)]**.

With increasing further the amount of the acid, the strong visible band decreases in intensity and a new band appears at 500 nm. The color was changed from red-purple to pink. This spectral behavior is similar to that of a catecholate Ni (II) complex with diphenylphosphinoethane as a co-ligand, indicating that protonation of the dioxolene moiety occurs (Figure 3 (c)). In the electrochemical measurement, the reduction wave of the Ni (II/I) decreased and a new wave was observed at –1.12 V vs Ag/Ag$^+$ upon addition of acid. This result clearly demonstrates that the protonation of the dioxolene moiety induces a significantly positive shift of the Ni (II/I) reduction potential.

Upon addition of trifluoromethanesulfonic acid, **[Ni(azocat)$_2$]** showed a photo-response, which is similar to that of **[Ni(azocat)(dppe)]**. With increases in the amount of acid, the band at 410 nm decreased in intensity, and a new strong band appeared in the visible region. With further addition of acid, the strong visible band decreased in intensity, and a new band appeared at 500 nm.

It is noteworthy that the protonation of the azo-conjugated metalladithiolene is needed with the more acid than that of the azo-conjugated dixolene. The difference is caused by higher ability of the electron-donation to the azo moiety for the dixolene compared with the dithiolene.

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