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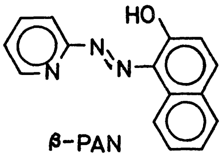
BIVALENT COBALT COMPLEXES WITH 1-(2-PYRIDYLAZO)-2-NAPHTHOL (β-PAN) AND ANALOGOUS LIGANDS

Katsura MOCHIZUKI and Masatoshi FUJIMOTO*
Department of Chemistry, Faculty of Science,
Hokkaido University, Sapporo 060

Bivalent cobalt complexes with the title ligands were synthesized and isolated. They were characterized by absorption spectra and magnetic moments. The Co(II) complexes were found to be oxidized to the Co(III) complexes in DMSO in the presence of Cu(II) ions.

In the reactions between Co(II) ion and the title ligands in aqueous media, Co(II) complexes formed are immediately oxidized to the corresponding Co(III) complexes.[1-3] Therefore it is difficult to investigate characters of Co(II) complexes. The isolation of Co(II) complex with β-PAN has not been reported so far.[3] Though Pandeya et al. synthesized the pink colored cobalt(II) complex with an analogous ligand, 10-(2-pyridylazo)-9-phenanthrol (PAPhen), an ambiguity remains on the composition of the reported complex with 4 mols of ethanol and 1/3 mol of chloroform.[4] In the present study we synthesized, first isolated, and characterized bivalent cobalt complexes with β-PAN, 2-(2-pyridylazo)-1-naphthol (α-PAN), and also PAPhen.

Synthesis of Co(II) complexes. 1) Free acid form of α-PAN (1.0 g) and ascorbic acid (1.0 g) were completely dissolved in ethanol (500 cm^3) by heating under nitrogen atmosphere. To the solution $CoCl_2$ (0.26 g) dissolved in a small amount of ethanol was added. The mixture was stirred and kept at 50 °C for 1.5 h. The green product formed was filtered, washed with ethanol, and dried in vacuo (yield 1.25 g). The green complex of a definite composition was always obtained under the above conditions. Found: C, 54.51; H, 3.74; N, 10.86; Cl, 6.62%. Calcd for $C_{30}H_{20}N_6O_2Co\cdot C_6H_8O_6\cdot(3/2)HCl$: C, 54.99; H, 3.78; N, 10.69; Cl, 6.76%. IR spectrum of the green complex shows the bands corresponding to ascorbic acid around 1753 and 1650-1680 cm^{-1}. The magnetic moment μ_{eff} at 300 K is 1.94 BM. ESR measurements show no signals of organic radicals. Above data suggest that the green complex is a bivalent cobalt complex, though the state of ascorbic acid in the green complex and the structure of the green complex are not clear. A similar product was obtained for PAPhen by the analogous method. Found: C, 58.78; H, 3.87; N, 9.77%. Calcd for $C_{38}H_{24}N_6O_2Co\cdot C_6H_8O_6\cdot 2HCl$: C, 57.29; H, 3.89; N, 9.54%.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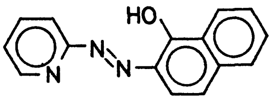
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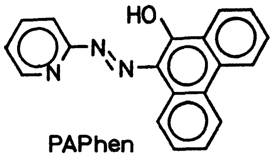
PAPhen

2) To an ethanol solution (500 cm^3) of the green complex (1.0 g), metal sodium (0.1 g) dissolved in ethanol (5 cm^3) was added. The solution turned red immediately. The red complex precipitated by evaporation was filtered, washed with ethanol thoroughly, recrystallized from ethanol-chloroform (1 : 1 v/v) several times, and dried in vacuo (yield ca. 60%). The red complex is more soluble in non-polar solvents such as chloroform than in ethanol and insoluble in water, indicating itself acting as a noncharged complex. ESR measurements at 77 K show the signal of Co(II) ion for the red complex, whereas no signal appeared for $[Co^{III}(\beta\text{-pan})_2]Cl$. Red complexes, $[Co^{II}(\alpha\text{-pan})_2]$ and $[Co^{II}(\text{paphen})_2]$, were also synthesized by the analogous method. The data of elemental analysis for red complexes are listed in Table 1 together with the color and the shape of crystals. The data of elemental analysis for $[Co^{II}(\beta\text{-pan})_2]$ and $[Co^{II}(\alpha\text{-pan})_2]$ agree with those for the complexes with (1/4)NaCl (hereafter (1/4)NaCl is omitted).

Characterization of red complexes. The data of absorption spectra in $CHCl_3$ and magnetic moments (solid) at room temperature for red complexes are listed in Table 2. The absorption spectrum of $[Co^{II}(\beta\text{-pan})_2]$ is the same as the spectrum of the Co(II) complex observed in the rapid-scan spectral study of the reaction between Co(II) ion and β-PAN1) and in the reduction product of $[Co^{III}(\beta\text{-pan})_2]Cl$ by O_2^- ion.5) Though the absorption spectra of these complexes do not change in an aprotic solvent, DMSO, even bubbled with O_2 stream for ca. 30 min. When a small amount of water (0.5 cm^3 H_2O to 3.5 cm^3 DMSO) is added to the above solutions, the absorption spectra change immediately to those corresponding to the Co(III) complexes. Data of elemental analysis and the absence of absorption bands for Co(III) complexes in spectra of the isolated complexes measured in $CHCl_3$ indicate that isolated complexes do not contain Co(III) complexes. These results support the success in the isolation of Co(II) complexes with these ligands.

Magnetic moments of the red complexes also show that these complexes are not Co(III) complexes but Co(II) complexes with more than one spin. It is well known that μ_{eff} of a Co(II) complex is variable depending on its spin-state and coordination number and geometry.6) For example, the values of μ_{eff} are expected to be 5.0-5.8, 1.80-1.85, and 2.2-2.9 BM, for octahedral high-spin, octahedral low-spin, and four-coordinated low-spin Co(II) complexes, respectively.6) The values of μ_{eff} for these complexes in Table 2 are smaller than those for octahedral high-spin complexes and larger than those for octahedral low-spin complexes. This anomalous magnetic moment would be interpreted as follows: 1) Mixture of high-spin Co(II) complexes and diamagnetic Co(III) complexes, 2) four-coordinated low-spin complexes, or 3) spin-state equilibrium between ^2E_g and $^4T_{1g}$ states. 1) is excluded from results of absorption spectra and elemental analysis as mentioned above. The other possibilities remains; temperature-dependence of magnetic moments should be necessary to decide which one is taken. From the results of temperature-dependence of magnetic moment for $Co^{II}(\text{paphen})_2 \cdot 4EtOH \cdot (1/3)CHCl_3$ (pink complex), Pandeya et al. considered the spin-state equilibrium between ^2E_g and $^4T_{1g}$.4) Though the composition of the complex used in their study is ambiguous and different from the complex synthesized in the present study, the similarity of our data to their data suggests that the existence of the spin-state equilibrium is also expected in the case of the other red complexes, [Co^{II}(β-pan)$_2$] and [Co^{II}-(α-pan)$_2$]. In any case, the binding states between ligands and Co(II) ion in Co(II) complexes are expected to be considerably flexible, whereas Co(III) complexes have rigid structures.$^{7)}$

As the formation of stable 1 : 1 Cu(II) complexes with these ligands in DMSO were found from molar-ratio method,$^{8)}$ the metal substitution reactions were anticipated by the addition of a large excess of Cu(II) ions. Contrary to anticipations, the substitution reactions and also a reversed substitution of Cu(II) ion from [Cu^{II}(β-pan)(OH$_2$)]$^+$ by a large excess of Co(II) ions in DMSO were

Table 1. Elemental analysis, the color, and the shape of crystals of red complexes

Complex	Found (Calcd) (%)				Color	Shape
	C	H	N	Cl		
[Co^{II}(β-pan)$_2$]	63.52	3.65	14.39	1.27	deep red purple	too fine to identify
$C_{30}H_{20}N_6O_2Co\cdot(1/4)NaCl$	(63.21)	(3.54)	(14.74)	(1.55)		
[Co^{II}(α-pan)$_2$]	63.17	3.65	14.83		dark purple	rhombus (plate)
$C_{30}H_{20}N_6O_2Co\cdot(1/4)NaCl$	(63.21)	(3.54)	(14.74)			
[Co^{II}(paphen)$_2$]	68.04	3.59	12.87		deep red purple	rhombus (plate)
$C_{38}H_{24}N_6O_2Co$	(69.62)	(3.69)	(12.82)			

Table 2. Data of absorption spectra and magnetic moments

Complex	λ_{max}/nm	ε/10^4 mol^{-1} dm^3 cm^{-1}	μ_{eff}/BM at 297 K
[Co^{II}(β-pan)$_2$]	522	2.83	2.31
[Co^{II}(α-pan)$_2$]	322	2.80	2.16
	545	3.44	
[Co^{II}(paphen)$_2$]	310	3.38	2.52
	520	3.74	

not observed. The red solutions of Co(II) complexes in DMSO change to green by adding Cu(II) ions as perchlorates; the same changes were observed by the addition of other Cu(II) salts. The spectra of the final products correspond to those for the Co(III) complexes. The effect of perchlorate ions is neglected, since no changes in the spectra of Co(II) complexes were observed by the addition of perchlorates of other metals such as Zn(II). The oxidation by Cu(II) ions should form Cu(I) ions. The difference of the spectrum of the mixed solutions of the final products and 2,2'-biquinoline and that of the final products gave the spectrum of Cu(I)-2,2'-biquinoline complex, indicating the presence of Cu(I) ions in the solutions of final products formed in the reactions between red complexes and Cu(II) ions. These facts reveal the oxidation of Co(II) complexes to the Co(III) complexes in the presence of Cu(II) ions in DMSO media.

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