Stability Order in Metal Chelate Compounds. III.[1]
*4-Nitro- and 4-Chlorocatechol Complexes**

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In view of the relatively high stabilities of the zinc(II) chelates of the catechol derivatives,[2] it was decided to investigate the interaction of bivalent transition metal ions with other catechol derivatives. The ligands employed in the present work are 4-nitro- and 4-chlorocatechol. Since both the nitro and the chloro group, as well as the sulfonate and carboxylate groups, are known to act as electron-withdrawing substituents, the extent of the effects of these substituents on the chelate stability and on the dissociation of catechol protons is estimated.

Experimental

The preparation of metal solutions, and the apparatus and procedures for potentiometric titration, have been mentioned elsewhere.[2,3]

4-Nitrocatechol.[4] — Into a mixture of catechol and sodium nitrite dissolved in water was added 2.5 M sulfuric acid at 0°C with stirring. After the addition of sulfuric acid had been completed, the reaction mixture was treated with ether; the product was recovered from the ether extract. The yellow needle-like crystals were recrystallized from benzene and purified further by vacuum sublimation at 1 mmHg and 130~140°C; m. p.: found, 176~177°C; reported,[4] 172~174°C.

Found: C, 46.40; H, 3.15; N, 9.20. Calcd. for $C_6H_5O_4N$: C, 46.46; H, 3.25; N, 9.03%.

4-Chlorocatechol.[5]—Sulfuryl chloride was added gradually to an ether solution of catechol at nearly 0°C. The reaction mixture was stirred for approximately one hour at 0°C, and then the crude material was recovered as ether was removed from the solution under reduced pressure. This material was recrystallized from benzene as white crystals; m. p.: found, 87.2~88.2°C; reported,[6] 88°C.

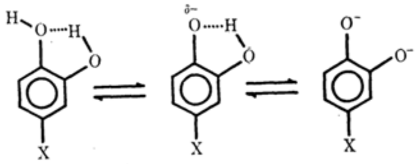
Found: C, 50.03; H, 3.47. Calcd. for $C_6H_5O_2Cl$: C, 49.85; H, 3.49%.

Results and Discussion

Acid Dissociation Constants.—The dissociating catechol protons of both 4-nitro- and 4-chlorocatechol were found to behave in a manner similar to those of catechol derivatives reported previously.[2] The acid dissociation constants of the present catechols are summarized in Table I. It is obvious that the nitro group situated at the 4-position has a profound electron-withdrawing effect on the dissociation of catechol protons, thus lowering both pK_{H_2L} and pK_{HL} values. Therefore, the dissociation of the protons of 4-nitrocatechol must take an alternative process to that assumed for the 4-sulfo and 4-carboxy derivatives,[2] as is shown in Chart 1. Meanwhile, since the chloro group exerts a greater electron-withdrawing effect at its meta position than at the para, 4-chlorocatechol must undergo the same dissociation as the nitro derivative.

TABLE I. ACID DISSOCIATION CONSTANTS OF THE CATECHOLS
$30\pm0.1°C$, $\mu=0.10$ M (KNO_3)

Ligand	pK_{H_2L}	pK_{HL}
4-Nitrocatechol	6.59	10.75
4-Chlorocatechol	8.43	11.54



$X=NO_2$, Cl

Chart 1. Dissociation process of catechol-protons.

Chelate Stability Constants. — The stability constants for the bivalent metal chelate compounds with the two catechol derivatives of the present study are summarized in Table II. Among the metal chelates of catechol derivatives studied in these laboratories, the following stability order with respect to a ligand was established:

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[1] Part II: Y. Murakami and M. Takagi, This Bulletin, 37, 268 (1964).

[2] Y. Murakami, K. Nakamura and M. Tokunaga, ibid., 36, 669 (1963).

[3] Y. Murakami, ibid., 35, 52 (1962).

[4] D. H. Rosenblatt, J. Epstein and M. Levitch, *J. Am. Chem. Soc.*, 75, 3277 (1953).

[5] R. Willstätter and H. E. Müller, *Ber.*, 44, 2182 (1911).

[6] J. Frejka, B. Šefránek and J. Zika, *Collection Czechoslov. Chem. Commun.*, 9, 238 (1937).

TABLE II. STABILITY CONSTANTS OF THE BIVALENT METAL CHELATES OF CATECHOL DERIVATIVES

30±0.1°C, μ=0.10 M (KNO_3)

Ligand	4-Nitrocatechol			4-Chlorocatechol		
	$\log K_1$	$\log K_2$	$\log K_3$	$\log K_1$	$\log K_2$	$\log K_3$
Zn(II)	8.20	6.80		8.63	6.82	
Cu(II)	11.65	9.28		12.56	9.83	
Ni(II)	7.82	5.27	3.81	7.90	5.00	4.16
Co(II)	7.48	5.31	3.14	7.64	6.37	4.23
Mn(II)	6.51	4.74		6.82	4.66	

4-nitrocatechol < catechol < 4-chlorocatechol ∼ 4-carboxycatechol < 4-sulfocatechol < Tiron.

There has been found no systematic relationship between the ligand basicity and the chelate stability, partly because of the difference between the dissociation process of the present ligands and that previously reported.²⁾ It is interesting to note that the 4-nitrocatechol chelates show relatively large stability constants for the lower basicity of the ligand. This is presumably due in part to the resonance contribution of the nitro group to the stabilization of the chelate ring.

The stability order among the transition metals treated in this work was found to be the same as that previously reported;²⁾ it follows the sequence:

manganese(II) < cobalt(II) ∼ nickel(II) < zinc(II) < copper(II).

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