formula Mo(OH)$_2$(CN)$_4^{2-}$ has been assigned.[9] The red complex affords the minimum of constraints on Mo–O multiple bonding, but with the concomitant liability of a resultant charge so large as to require the species to be stabilized in the ordered positive field provided by the cations in a crystalline arrangement.[24] The decided preference of the Mo(IV) and oxide oxygen atoms for uninhibited double bonding is most clearly suggested by one outstanding feature of the crystalline structure of NaK$_3$MoO$_2$(CN)$_4 \cdot 6$H$_2$O. Each oxygen atom of the complex anion is strongly hydrogen-bonded to two (w$_g$) water molecules of the partially hydrated sodium ion so that the transfer of any one of four protons from a w$_g$ molecule to a complexed oxygen atom, a jump of only 0.70 Å for the proton, would transform the red MoO$_2$(CN)$_4^{4-}$ into the blue MoO(OH)(CN)$_4^{3-}$ species. Although a statistical distribution of the protons between the two classes of positions thus defined would contribute entropic stabilization without detriment to the structural integrity of the arrangement, it appears that a fully ordered structure is required by energetic considerations in which Mo=O double bonding plays a critical role.

Partial collapse of the crystalline arrangement, engendered by the loss of the weakly held water molecules of w$_s$ type (*vide supra*), presumably would stimulate proton transfer from the w$_g$ water molecules to the complex anion and thus provide a general mechanism for dehydrative hydrolysis—a phenomenon reported for crystals of the potassium salt when these are maintained in a desiccator over concentrated sulfuric acid.[5,9] The precise course and the final products of such dehydrative hydrolysis of crystalline K$_4$MoO$_2$(CN)$_4 \cdot 6$H$_2$O remain in doubt; the earlier study[5] specified a color change from red to blue, suggesting formation of the MoO(OH)(CN)$_4^{3-}$ species, whereas Lippard and Russ[9] report a dull green or yellow-green product that suggests the presence of the Mo(OH)$_2$(CN)$_4^{2-}$ species.

The structure determination detailed herein serves to underwrite, in large measure, the conclusions drawn by Lippard and Russ from their study of the oxocyano and hydroxocyano complexes of molybdenum(IV). Perhaps the most interesting conclusion, negative though it be, is that the "classical" eight-coordinate Mo(OH)$_4$(CN)$_4^{4-}$ complex is not a stable species either in crystalline phases or in aqueous solution. This instability is not primarily attributable to the steric limitations imposed by the geometry of eight-coordination, but seems rather to arise from the energetic preference for just two molybdenum–oxygen bonds carrying each the maximum bond order.

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[24] A clear-cut example of excessive resultant charge producing instability in aqueous solution of a sterically excellent complex is provided by the octafluorotantalate(V) ion. The antiprismatic TaF$_8^{3-}$ ion, with Ta–F ~ 1.98 Å, is stabilized by sodium ion in the excellent Na$_3$TaF$_8$ crystalline structure,[25] but it gives way completely in aqueous solution to the heptafluorotantalate(V) species,[26] TaF$_7^{2-}$, in a configuration[27] (C$_{2v}$ monocapped trigonal-prismatic) that represents but little reduction in the closed-shell nonbonding interactions.

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Equilibria of Metal Ions with Pyrocatechol and 3,5-Di-*t*-butylpyrocatechol[1,2]

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Contribution from the Department of Chemistry, Illinois Institute of Technology, Chicago, Illinois. *Received August 7, 1967*

Abstract: The equilibrium constants from the reaction of Mn(II), Fe(II), Co(II), Ni(II), Cu(II), and Zn(II) ions with pyrocatechol in aqueous solution, and with pyrocatechol and 3,5-di-*t*-butylpyrocatechol in 50% methanol, have been studied potentiometrically, and those obtainable by this method are reported. Ultraviolet spectra of the manganese(II)- and copper(II)-pyrocatechol systems are consistent with the aqueous equilibria determined potentiometrically involving the formation of 1:1 and 1:2 chelates. The first protonation constant of pyrocatechol is determined more accurately than has previously been reported, resulting in the calculation of better values of the corresponding metal chelate formation constants. Differences in the nature of the complexes formed in 50% methanol, and the lower rate of complex formation, are ascribed to the greater basicity of the mixed solvent. Explanations are offered for the variety of metal ion complexes formed with 3,5-di-*t*-butylpyrocatechol. The results obtained indicate that manganese 3,5-di-*t*-butylpyrocatechol may serve as a model for the study of pyrocatechol autoxidation mechanisms.

Preliminary to an investigation into the mechanism of the metal-catalyzed oxidation of pyrocatechols, equilibria were studied in aqueous and 50% methanol–water solvents for pyrocatechol and 3,5-di-*t*-butylpyrocatechol complexes of Zn(II) and of first-row transition metals. Previous work on equilibrium and stability constants for Cu^{2+}–,[4–9] Zn^{2+}–,[7] and Fe^{3+}–pyrocate-

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Table I. Proton Association Constants of Pyrocatechol and 3,5-Di-*t*-butylpyrocatechol

Ligand	Medium	Ionic strength	Temp, °C	Log K_2^H	Log K_1^H	Ref
Pyrocatechol	Aqueous	0 (KCl)	25	9.45		5
		0	25	9.45	12.8	5
		0.06	25	9.15	11.23	27
		0.1 KNO_3	30	9.13	11.59	7
		0.1–0.15 $NaClO_4$	20	9.43	13.0	6
		0.1 (KCl)	25	9.37	12.8	28
		0.1 $NaClO_4$	20–25	9.37	13.6	29
		0.1 KNO_3	25	9.20	11.93	9
		0.857 KCl	25	9.177		4
		1.0 KNO_3	25	9.229	13.05	This work
		3.151 KCl	25	9.386		4
	50% methanol	0.1 KNO_3	25	10.012	14.1	This work
3,5-Di-*t*-butylpyrocatechol	50% methanol	0.1 KNO_3	25	10.354	14.7	This work
Pyrocatechol	100% methanol	1.0 $N(CH_3)_4Cl$	20	13.15	15.5	30

chol[10] systems have been reported for solutions of ionic strength up to 0.1 *M*. The potentiometric method used here has been applied to a limited extent to alcohol–water solvents.[11–14] Titanium(IV) is the only metal for which stability constants of pyrocatechol in methanol–water solvents have been determined, but the form of the complexing ligand (HL^- or L^{2-}) has not been resolved experimentally.[15]

Experimental Section

Reagents. Metal salts were Baker Analyzed and Fisher Certified Reagent grades, chosen on the basis of highest reported purity, and used without recrystallization. Potassium nitrate was reagent grade, twice recrystallized from water. Lithium perchlorate was made by allowing Li_2CO_3 to react with 70% $HClO_4$.[16] Pyrocatechol was supplied by Eastman Organic Chemicals and was sublimed once under vacuum before use. The 3,5-di-*t*-butylpyrocatechol was purchased from Gallard-Schlesinger Chemical Mfg. Corp., Carle Place, N. Y., and was recrystallized twice from benzene to a final melting point of 98.5–99.3° (lit.[17] 99.0°). Methanol was 99.9 mol % pure, obtained from Fisher Scientific, and used directly. Water was redistilled from a glass distillation apparatus and boiled 1 hr to remove CO_2. Water samples gave negative tests for oxidizable impurities by iodometry. Solutions of NaOH and HCl were made up to volume from vials supplied by British Drug Houses, Ltd., with redistilled water and stored under prepurified nitrogen (Matheson Chemical Co.), bubbled slowly through twin chromous chloride solutions, in automatic burets sealed to the atmosphere. Titrants and stock solutions in mixed solvent were made up to volume at 20° with equal weights of methanol and water.

Potentiometric Method. The potentiometric investigations were carried out in a glass cell wrapped in black tape to keep out light and water-jacketed for temperature control at 25.0 ± 0.01°. Both a Beckman Research pH meter and a Radiometer pH meter 4 were used. The former was particularly useful in detecting pH drifts, which frequently occurred in the systems studied, at rates as low as 0.00025 unit/min.

A Beckman E-2 glass electrode was used in aqueous solution with a frit junction calomel electrode (No. 39071). Beckman GP glass electrodes No. 41263 and No. 40498 both gave good results in 50% methanol in combination with the frit junction calomel, reproducible to the fourth place on the Beckman instrument. Fiber and frit junction potentials have been shown to be the same in this solvent mixture,[18] but the frit junction remains operational over much longer periods of time.

The pH scale was calibrated to read in units of $-\log [H^+]$ with HCl and NaOH in aqueous solution[19] and with trimethylolaminomethane (Tris)[20,21] as an additional standard in 50% methanol. The media were 1.0 *M* KNO_3 aqueous solution and 0.1 *M* KNO_3 50 wt % methanol–water. The equilibrium constants reported are therefore true thermodynamic constants relative to these reference states.

Metal ion stock solutions were prepared, stored under nitrogen, and used within the same day of preparation. These solutions were standardized complexometrically.[22] Samples of 100.00 ml were deaerated 1 hr in the potentiometric cell prior to titration, and a small positive nitrogen pressure was maintained.

Spectrophotometric measurements were taken with a Beckman DK-2 recording spectrophotometer at 25.0 ± 0.10° and a quartz, microaperture, 1-cm flow cell (Beckman No. 97290) against a variable-beam attenuator (Beckman No. 104185). Line connections with the potentiometric cell were made with Tygon and sterilized polyethylene and flushed with N_2 before the experimental solution was pumped through it. Spectra were taken with the flow off. Lithium perchlorate was substituted for KNO_3 because of the latter's strong absorption at 300 mμ.

Results

Protonation Association Constants. The pyrocatechol dianion protonates in aqueous medium in a two-step process according to the equations

$$H^+ + L^{2-} \rightleftharpoons HL^- \quad K_1^H = [HL^-]/[H^+][L^{2-}] \tag{1}$$

$$H^+ + HL^- \rightleftharpoons H_2L \quad K_2^H = [H_2L]/[H^+][HL^-] \tag{2}$$

K_1^H and K_2^H are the corresponding protonation association constants for the ligand, H_2L.

In pure water titration of pyrocatechol showed an isosbestic point at 276 mμ which held throughout the addition of 2 equiv of base, suggesting that only process 2 is occurring and ruling out the presence of any third species, including associated ones of the type reported

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Table II. Equilibrium Constants for Metal–Pyrocatechol Complexes in Aqueous Solution

Metal ion	Ionic strength	Temp, °C	$-\text{Log }{}^*K_1'$	$-\text{Log }{}^*K_1$	$-\text{Log }{}^*K_2$	Ref
Mn^{2+} (NO_3)	1.0 (KNO_3)	25	6.41	14.807	16.996	This work
Fe^{2+} (SO_4)	1.0 (KNO_3)	25	5.71	14.332	16.740	This work
Co^{2+} (Cl)	1.0 (KNO_3)	25	No	13.959 (10.57)[a]	15.856 (12.54)[a]	This work
Ni^{2+} (Cl)	1.0 (KNO_3)	25	No (5.3)[a]	13.511 (10.20)[a]	Ppt (12.42)[a]	This work
Cu^{2+}	0	25		8.11	11.76	5
	0.10–0.15 ($NaClO_4$)	20		8.18	8.78	6
	0.10 (KNO_3)	30		8.20	11.06	7
	0.10 (KCl)	25		8.41	11.42	8
	0.10 (KNO_3)	25		8.39		9
(SO_4)	1.0 (KNO_3)	25	No	8.679 (6.00)[a]	10.955 (7.79)[a]	This work
	0.785 (KNO_3)	25		8.625	10.999	4
	1.77 (KNO_3)	25		8.625	10.891	4
Zn^{2+}	0.1 (KNO_3)	30		12.26	13.94	7
(NO_3)	1.0 (KNO_3)	25	No	12.744 (9.76)[a]	14.315 (10.85)[a]	This work

[a] Equilibrium constants for 4,5-dihydroxybenzene-1,3-disulfonic acid (Tiron) in 1.0 *M* $NaClO_4$.[26]

at higher concentrations.[23] Potentiometric titration of 0.020 *M* pyrocatechol with 1.622 *N* NaOH with an E-2 electrode showed two distinct p*K* regions, separated by $\log K_1^H - \log K_2^H$ of 3.82 units, somewhat less than the 4.4 reported for Tiron in 1.0 *M* $NaClO_4$.[24–26] The values of K_1^H and K_2^H for pyrocatechol in 1.0 *M* KNO_3 are given in Table I, along with the results of other investigators.[4–7,9,27–30] The value of K_1^H in this work has been checked spectrophotometrically in the region of the second isosbestic point in 1.0 *M* $LiClO_4$ at 293 mμ.

The second protonation constants for pyrocatechol and 3,5-di-*t*-butylpyrocatechol in 50% methanol were obtained from $\bar{Z}$ *vs.* pH plots[31] at the $\bar{Z} = 0.5$ point. The ultraviolet spectra showed isosbestic points at 276 and 277 mμ, respectively, in this buffer region. The first protonation constant for pyrocatechol was estimated from ultraviolet shifts at high alkalinity to be $10^{14.1}$ and for 3,5-di-*t*-butylpyrocatechol, $10^{14.7}$. Since K_1^H in each case turned out to be so high and since solubility of the ligand complexes was low in 0.1 *M* and higher concentrations of KNO_3, higher ionic strengths were not studied.

Calculation of Metal–Ligand Equilibrium Constants. Metal–ligand equilibrium constants were determined for the following reactions

$$M^{2+} + H_2L \rightleftharpoons ML + 2H^+$$

$$^*K_1 = [ML][H^+]^2/[M^{2+}][H_2L] \quad (3)$$

$$ML + H_2L \rightleftharpoons ML_2{}^{2-} + 2H^+$$

$$^*K_2 = [ML_2{}^{2-}][H^+]^2/[ML][H_2L] \quad (4)$$

$$ML_2{}^{2-} + H_2L \rightleftharpoons ML_3{}^{4-} + 2H^+$$

$$^*K_3 = [ML_3{}^{4-}][H^+]^2/[ML_2{}^{2-}][H_2L] \quad (5)$$

Here M^{2+} represents the metal ion and H_2L is the ligand. With the usual material balance expressions, eq 3–5 may be solved as

$$^*K_n = \frac{(T_L - [H_2L]x - (n-1)T_M)[H^+]^2}{(nT_M - T_L + [H_2L]x)[H_2L]} \quad (6)$$

where $[H_2L] = (2T_L - T_{OH} - [H^+] + [OH^-])/\{2 + (K_2^H[H^+])^{-1}\}$. Here T_L and T_M are the total analytical concentrations of metal ion and ligand, respectively, T_{OH} = molar concentration of added NaOH, and $x = 1 + 1/K_2^H[H^+]$.

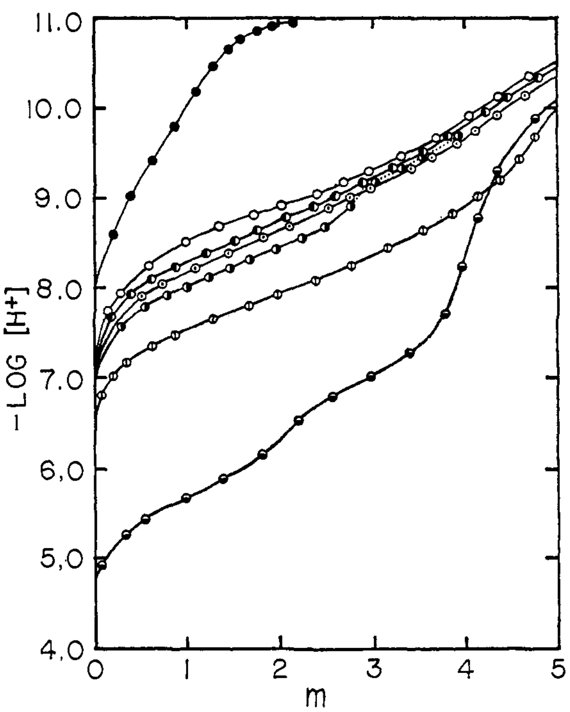

Figure 1. Potentiometric titration curves for M^{2+}–pyrocatechol (1:3) complexes (1.0×10^{-3} *M* M^{2+}) in 1.0 *M* KNO_3 aqueous solution at 25°: ●, ligand (1×10^{-3} *M*); ⊖, Zn^{2+}; ◒, Cu^{2+}; ◑, Ni^{2+}; ⊙, Co^{2+}; ◐, Fe^{2+}; ○, Mn^{2+}. Dotted line indicates precipitate present.

In mixed solvent, in addition to the above reactions, the reaction $M^{2+} + 2H_2L \rightleftharpoons M(HL)_2 + 2H^+$ was also found to occur. The equilibrium expression for this reaction was derived as

$$^*\beta_2' = \frac{(T_L - [H_2L]x)[H^+]^2}{(2T_M - T_L + [H_2L]x)[H_2L]^2} = \frac{[M(HL)_2]}{[M^{2+}](K_2^H)^2[HL^-]^2} \quad (7)$$

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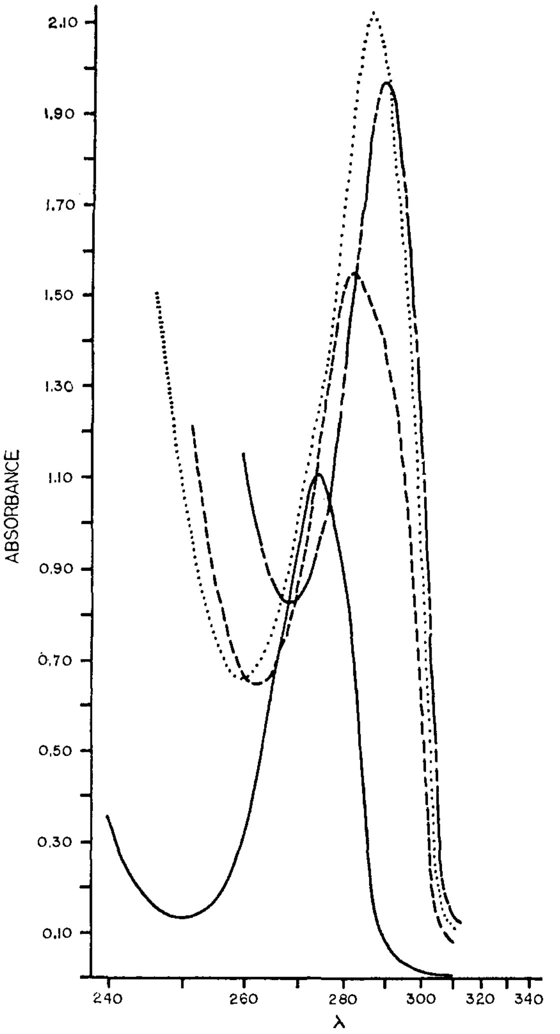

Figure 2. Uv spectra of Cu^{2+}–pyrocatechol (1 : 1) at various stages of titration: ——, $m = 0$; – – – –, $m = 1.0$; · · · ·, $m = 1.5$; — — — —, $m = 2.0$. ($T_M = T_L = 6.8 \times 10^{-4}$ M, 1.0 M $LiClO_4$ aqueous solution at 25°.)

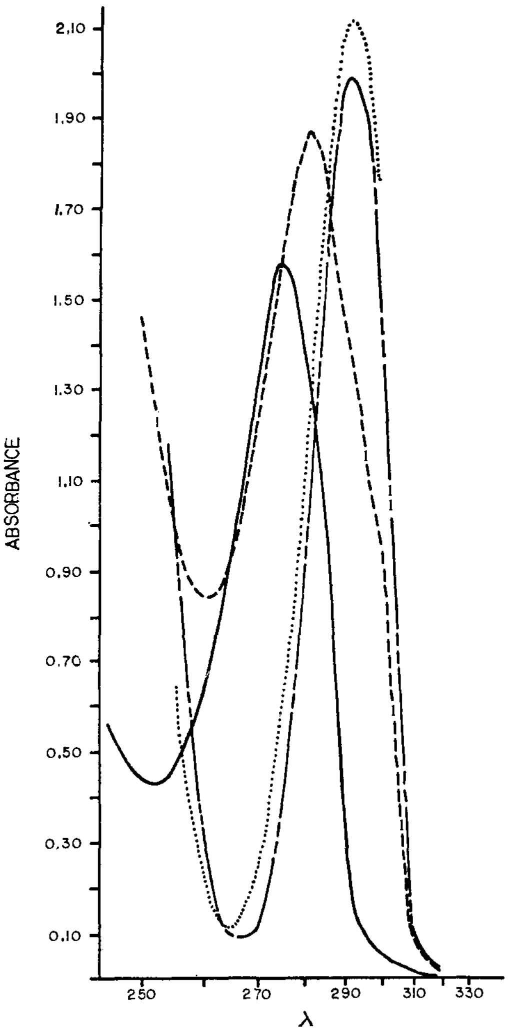

Figure 3. Uv spectra of Cu^{2+}–pyrocatechol (1 : 2) at various stages of titration: ——, $m = 0$; – – – –, $m = 1.0$; — — — —, $m = 2.0$; · · · ·, $m = 4.0$. ($2T_M = T_L = 6.2 \times 10^{-4}$ M, 1.0 M $LiClO_4$ aqueous solution at 25°.)

The equilibrium constant for formation of the protonated complex $M(HL)^+$ is expressed by $*K_1'$

$$M^{2+} + H_2L \rightleftharpoons M(HL)^+ + H^+$$

$$*K_1' = [MHL^-][H^+]/[M^{2+}][H_2L] \quad (8)$$

Aqueous Equilibrium Constants. Potentiometric equilibrium curves for Mn^{2+}–, Fe^{2+}–, Co^{2+}–, Ni^{2+}–, Cu^{2+}–, and Zn^{2+}–pyrocatechol systems containing a 3 : 1 molar ratio of ligand to metal ion are shown in Figure 1. In the case of Ni^{2+}, a fine brown precipitate settled out very slowly above $m = 2$ (m = number of moles of NaOH added/mole of metal ion).

Equilibrium constants for these complexes are listed in Table II. Previously reported results by Nasanen and Markkanen[4] give $-\log *K_1$ and $-\log *K_2$ for Cu^{2+}–pyrocatechol as 8.625 and 10.999, respectively, for an ionic strength of 0.785, and 8.625 and 10.891 for $\mu = 1.77$ in KNO_3, in good agreement with the 8.679 and 10.955 values in 1.0 M KNO_3 in this work. Values of equilibrium constants for metal–Tiron chelates are also included for comparison.

Protonated 1 : 1 complexes of the type $M(HL)^+$ were not detected except for narrow regions of low "m" values ($m = 0.25$) in the Mn^{2+} and Fe^{2+} titrations. Such complexes have been reported for UO_2^{2+} [29] and are indicated for titanium(IV) in acidic solutions.[15b] The equilibrium constants obtained for these complexes are not as accurate as those obtained for ML and ML_2 formation but are included in Table II. Complexes of the type $MLHL^-$ and $M(HL)_2$ could not be detected for the aqueous systems.

Figures 2 and 3 show the spectra for the 1 : 1 and 1 : 2 Cu(II)–pyrocatechol systems, respectively, at progressive stages of formation. In both cases a shift to 292 mμ (+17 mμ) is observed at the stoichiometric end point and, in conjunction with potentiometric data, indicates that only CuL or CuL_2^{2-} are present under the conditions employed.

Figures 4 and 5 show uv spectra for 1 : 1 and 1 : 2 Mn(II)–pyrocatechol titrations. A 1 : 1 complex is clearly in evidence at the end point of the 1 : 1 run. In the 1 : 2 case, however, after 4 equiv of NaOH was added, the peak was still broad and had shifted only to 282 mμ. The new peak is not unequivocally assigned. It could conceivably be due to an $M(HL)_2$ type complex but is more likely a composite of a peak at 275 mμ (uncomplexed ligand), a peak at 292 mμ (ligand complexed as ML), and one at 292 mμ (HL^-). When excess NaOH was added (to about pH 11.5) the peak narrowed and a new maximum appeared at 291 mμ,

Table III. Equilibrium Constants for Metal–Ligand Reactions in 50% Methanol (0.10 M KNO_3, 25.0°)

Metal ion	Ligand	Equilibrium quotient	Symbol	−Log K
Mn^{2+}	Pyrocatechol	$[M(OH)(HL)][H^+]^2/[M^{2+}][H_2L]$	$*K_1'(OH)$	14.66 ± 0.02
Mn^{2+}	Pyrocatechol	$[M(HL)_2][H^+]^2/[M^{2+}][H_2L]^2$	$*\beta_2'$	11.46 ± 0.01
Mn^{2+}	3,5-Di-*t*-butyl-pyrocatechol	$[M(OH)(HL)][H^+]^2/[M^{2+}][H_2L]$	$*K_1'(OH)$	14.68 ± 0.01
Mn^{2+}	3,5-Di-*t*-butyl-pyrocatechol	$[M(HL)_2][H^+]^2/[M^{2+}][H_2L]^2$	$*\beta_2'$	12.23 ± 0.01
Cu^{2+}	Pyrocatechol	$[ML][H^+]^2/[M^{2+}][H_2L]$	$*K_1$	7.85 ± 0.01
Cu^{2+}	Pyrocatechol	$[ML_2{}^{2-}][H^+]^2/[ML][H_2L]$	$*K_2$	9.02 ± 0.01
Cu^{2+}	3,5-Di-*t*-butyl-pyrocatechol	$[M(HL)^+][H^+]/[M^{2+}][H_2L]$	$*K_1'$	0.94 ± 0.01

indicating formation of a complex of the type $ML_2{}^{2-}$, as in the copper(II) case.

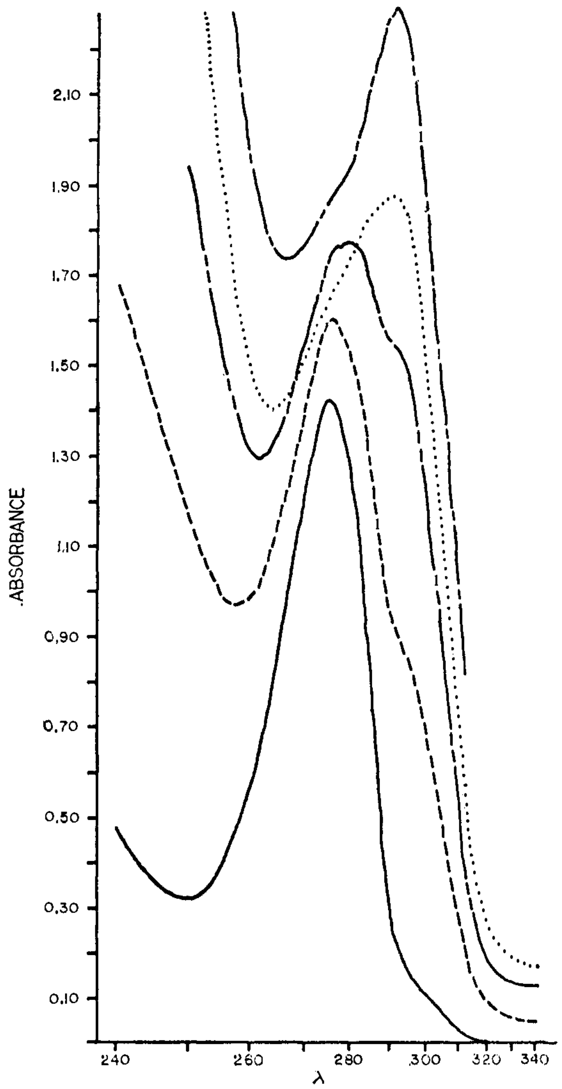

Figure 4. Uv spectra of Mn^{2+}–pyrocatechol (1:1) at various stages of titration: ——, m = 0; - - - -, m = 0.5; — - - —, m = 1.0; · · · ·, m = 1.5; — - —, m = 2.0. ($T_M = T_L = 5.9 \times 10^{-4}$ M, 1.0 M $LiClO_4$ in aqueous solution at 25°.)

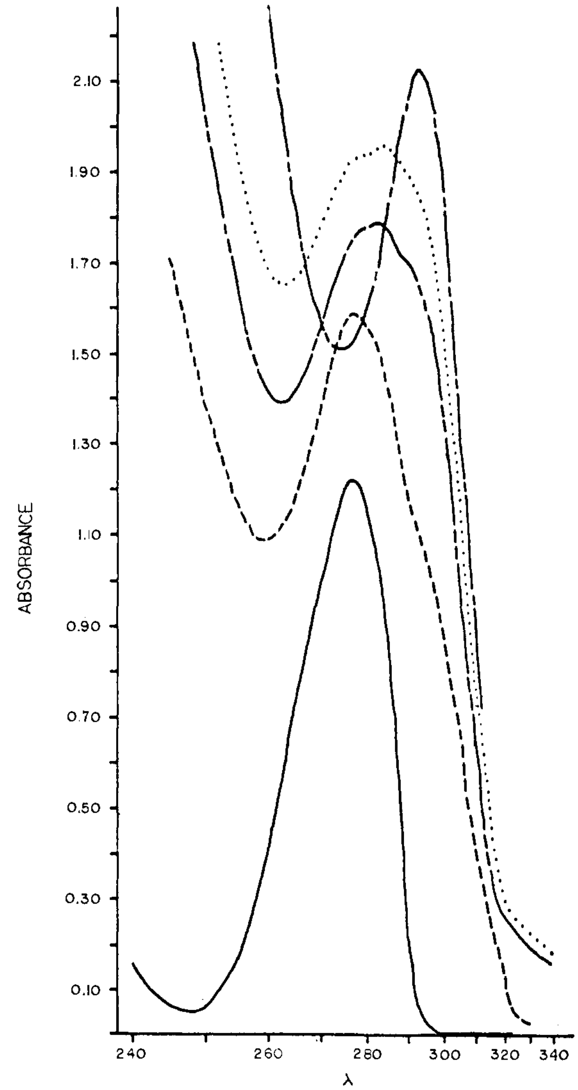

Figure 5. Uv spectra of Mn^{2+}–pyrocatechol (1:2) at various stages of titration: ——, m = 0; - - - -, m = 1.0; — - - —, m = 1.72; · · · ·, m = 2.0; — - —, m = 16.4 (pH ~11.5). ($2T_M = T_L = 6.9 \times 10^{-4}$ M, 1.0 M $LiClO_4$ aqueous solution at 25.0°.)

Equilibrium Constants for the Methanol–Water Solvent System. The same metal ions were studied in 50% methanol as in water with both pyrocatechol and 3,5-di-*t*-butylpyrocatechol. The complexes for which equilibrium constants could be determined are given in Table III. An ion product of 1.34×10^{-14} was used, derived from the activity coefficients for 0.1 M HCl[32] and the autoprotolysis data of Koskikallio.[33] The Cu^{2+}–pyrocatechol system (Figure 6) gave titration curves in mixed solvent similar to those obtained in water, with clear-cut breaks at m = 2 and 4. A

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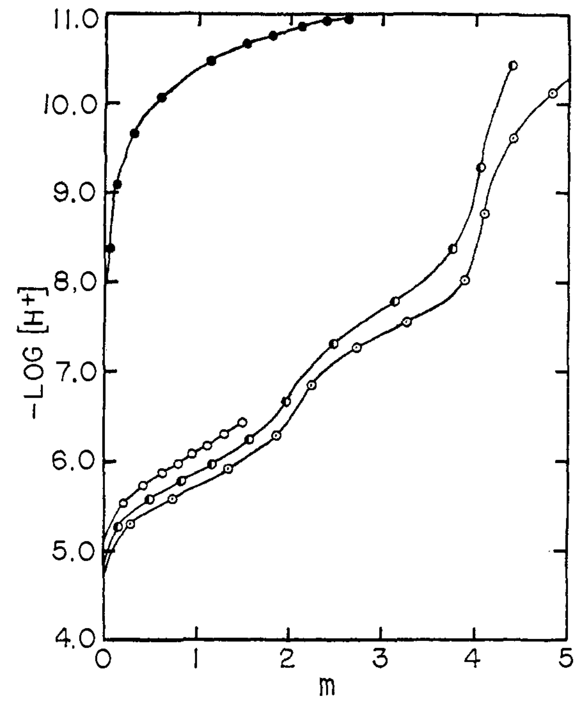


Figure 6. Potentiometric titration curves for Cu^{2+}–pyrocatechol (metal ion = 1 × 10^{-3} *M*) complexes in 50% methanol, 0.1 *M* KNO_3, 25°: ●, ligand (1 × 10^{-3} *M*); ○, 1:1; ◐, 1:2; ⊙, 1:3.

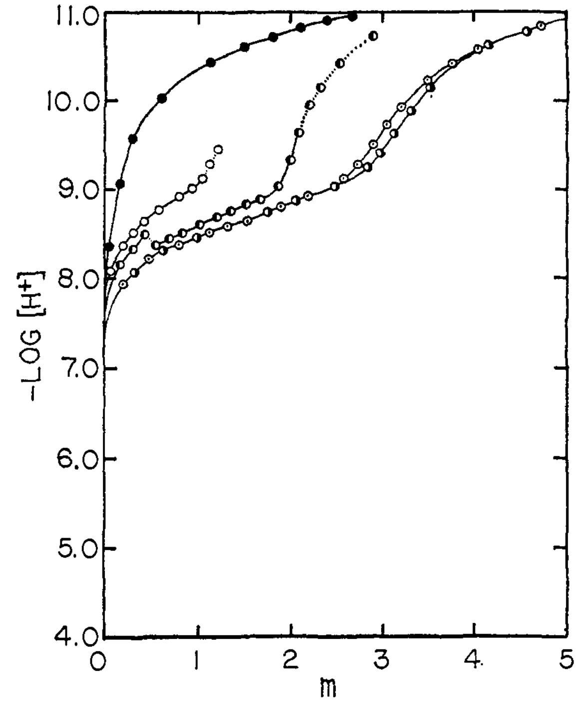


Figure 7. Potentiometric titration curves for Mn^{2+}–3,5-di-*t*-butylpyrocatechol complexes (metal ion = 1 × 10^{-3} *M*) in 50% methanol, 0.1 *M* KNO_3, 25.0°: ●, ligand (1 × 10^{-3} *M*); ○, 1:1; ◐, 1:2; ⊙, 1:3 (back titration with 0.1 *M* HCl); ◑, 1:3 (forward titration with 0.1 *M* NaOH). Dotted line indicates system not at equilibrium.

1:3 curve shows that the maximum coordination number for Cu^{2+} is 4. No pH drift, precipitation, or unusual color changes were observed throughout any of these titrations.

With Cu(II) and 3,5-di-*t*-butylpyrocatechol, yellow or blue-black precipitates resulted upon adding base. After a 2-day equilibration period titrations could be carried out with no apparent pH drift, and steady pH readings were obtained through to an end point at *m* = 1 for both 1:1 and 1:2 systems. During the initial equilibration period the solution changed from colorless to green, and finally to beautiful green-gold, the absorbance at 385 mμ increased 0.40 unit for the 1:1 system at 6.5 × 10^{-4} *M*, and the pH dropped 1.5 units. An apparent stability constant for a complex with the empirical formula $Cu(HL)^+$ was calculated from the potentiometric data after equilibration. In excess base a precipitate with approximate composition $Cu(HL)(NO_3)$ was obtained for both 1:1 and 1:2 cases.

Zinc formed insoluble colorless complexes with pyrocatechol throughout the *m* = 0–4 titration region, regardless of the time allowed for preequilibration. Above pH 11.0, a 1:3 solution, allowed to stand overnight, cleared up, showing a spectral shift from 276 mμ to 292 mμ, characteristic of formation of complexes of the ML type (+16 mμ for HL^- and 28 mμ for L^{2-} in this solvent mixture). With 3,5-di-*t*-butylpyrocatechol the solution remained colorless throughout, and only hydroxy complexes formed. Nickel(II) and cobalt(II) gave precipitates with both ligands. Iron(II) reacted with 3,5-di-*t*-butylpyrocatechol very slowly, more than 4 days being required for the pH to stop dropping after NaOH addition, but no precipitation occurred.

Only manganese(II) formed soluble complexes with 3,5-di-*t*-butylpyrocatechol within reasonable time periods. After each addition of base it was necessary to wait 2 to 3 hr for equilibrium up to the inflection point, after which the titration proceeded rapidly. The use of heat and other solvents, the use of auxiliary ligands, and changing reagent concentrations, metal–ligand ratios, or supporting electrolyte failed to eliminate the period required for equilibration.

With both pyrocatechol and 3,5-di-*t*-butylpyrocatechol inflections were observed at *m* = 1, 2, and 3 for 1:1, 1:2, and 1:3 titration curves, respectively, as shown for the Mn^{2+}–3,5-di-*t*-butylpyrocatechol system in Figure 7. Calculations were carried out on buffer regions involving the addition of up to 3 moles of base per mole of metal ion, depending on the ligand/metal ion ratio, and the equilibrium constants obtained are given in Table III.

Discussion

Previous investigators have reported low values of the first proton association constant K_1^H. In the present study a higher K_1^H value has been obtained from potentiometric and spectrophotometric measurements at an ionic strength of 1.0. It was still found possible to calculate constant values for the stability constants for all the metal ions with pyrocatechol using a value for K_1^H more than 1.0 log unit lower than the true one, because of the low concentration of the dianion and the constant value of $[L^{2-}]/[H^+]$ at the highest pH values studied.

If it is assumed that K_1^H of pyrocatechol shows the same trend with ionic strength as does Tiron,[24] the value of 13.05 is suggested as the minimum log value of K_1^H at 0.10 ionic strength. This conclusion is borne out by an approximate value of log K_1^H of 13.6 reported by

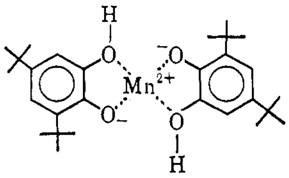
Bartusek and Sommer.[29] Since direct measurement of log K_1^H at these electrolyte concentrations is subject to a large error, being outside the region of constant ionic strength, the use of equilibrium constants, $^*K_n$, involving displacement of protons from the protonated ligand is preferred over the normal chelate formation constants.

From the results given in Table II, it is obvious that the stabilities in water conform to the Irving–Williams series with $Zn^{2+} > Ni^{2+}$. Undoubtedly, Mn^{2+}, Fe^{2+}, and Co^{2+} form 1:3 chelates at pH values higher than those in this study, since there are numerous instances of their isolation in the literature, and since more acidic pyrocatechols, such as tetrabromo- and tetrachloropyrocatechol, show sharp end points at $m = 6$ in 50% methanol when titrated in the presence of Mn^{2+}, with a 3:1 ligand/metal ion ratio. It is interesting to note that pyrocatechol forms one of the most stable complexes of a bidentate ligand with the Mn(II) ion.[34]

In 50% methanol, a variety of metal complexes are formed by 3,5-di-*t*-butylpyrocatechol. For the Mn(II)–3,5-di-*t*-butylpyrocatechol system, with molar ratios of ligand to metal equal to less than 1:1, a buffer region involving release of 2 equiv of hydrogen ion per mole of ligand was found potentiometrically (Table III), probably corresponding to the formation of species having the composition ML, or possibly M(OH)(HL). When fast titrations of these metal–ligand systems were carried out without waiting for the system to equilibrate between additions of base, equilibrium constants for the formation of $Mn(OH)^+$ were calculated for the titration curves up to the incidence of cloudiness in the solution. Since it is known that a hydroxyl group in the inner coordination shell can facilitate further substitution,[35] the possibility of the formation of mixed ligand complex, Mn(OH)(HL), could not be eliminated.

An attempt was made to resolve this question spectrophotometrically. The uv spectra of a 1:1 Mn(II)–3,5-di-*t*-butylpyrocatechol mixture showed an enhancement in intensity at the 279 mμ $\pi \rightarrow \pi^*$ absorption, and a small shift to the red, upon addition of 2 equiv of base. After several hours the peak had shifted only about 4 mμ and, after standing overnight in excess NaOH, the shift observed was still only 4.5 mμ to 283.5 mμ, far less than the +19-mμ shift expected for formation of the monoanion. By analogy with the aqueous spectra wherein the red shift was less for the dianion with metal ion present, this latter observation was taken as an indication that M(OH)(HL) might indeed be present. An attempt to verify this by observing the shift in Mn(II) d → d transitions (400 mμ) at higher concentrations in a 10-cm cell failed because of insufficient solubility. Hydrolysis of the metal ion is believed to be an important factor complicating the interpretations of Ti(IV)–pyrocatechol equilibria in mildly alkaline 50% methanol,[15] and the evidence available from the present study, although not conclusive, indicates that the same effect may be occurring here.

When the molar ligand/metal ratio was greater than 1:1, the potentiometric data indicated only the formation of the protonated complex, $M(HL)_2$. After addition of base, the absorption at 279 mμ is broader than in the 1:1 case, extending into the visible region. In excess base under conditions where only monoanion would be present, the maximum peak shift of the complex was to 293 mμ, which again would be consistent with the presence of protonated complex species. Analysis of the potentiometric data showed no evidence for the formation of an intermediate species MHL^+. From the data in Table III the $\Delta G°$ for this process would be −3.34 kcal/mole. The most likely formula for this complex would be



Its solution was green, a color reported to be characteristic of manganese tetrahedral complexes.[36] As far as it is possible to tell in view of the lower accuracy of the data, the same behavior applies to 50% methanol solutions of manganese(II)–pyrocatechol.

The marked contrast in the tendency of manganese to complex with pyrocatechol in the two solvents and the type of complexes formed were unexpected. The difference can be tentatively attributed to the more favorable change in entropy through neutralization of hydroxide ion in 50% methanol and might be considered as a manifestation of the so-called "basicity" effect[37] on changing from water to water–alcohol mixtures.

Copper(II) and 3,5-di-*t*-butylpyrocatechol appear to form a charge-transfer complex on standing under a nitrogen atmosphere in acidic solution. The main evidence for this conclusion is the appearance of a quinoid peak at 385 mμ without any significant change in the uv pyrocatechol peak. (No such peak was observed in the manganese case.) Furthermore, the precipitate formed from a 1:2 solution with excess base showed one ligand bound per copper ion rather than two, which would also be in keeping with the ability of the metal ion to form only one such complex. Upon precipitation of the complex with excess base, the filtrate was found to be colorless, indicating the absence of free *o*-quinone from the accidental leakage of oxygen into the system or from internal oxidation followed by release of the ligand to the solution, which might account for this new peak. Since the ligand is more readily oxidizable than pyrocatechol,[38,39] its behavior toward copper would not necessarily be the same. When a fast titration of the Cu(II)–3,5-di-*t*-butylpyrocatechol system was carried out, a peak at 298 mμ began to form before precipitation wiped it out. The dianion forms normal chelates with Cu(II) in strongly alkaline solution, as indicated by a spectral shift of the $\pi \rightarrow \pi^*$ transition to 298 mμ. The new peak at 298 mμ is broadened by overlap with one at lower wavelength.

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Zinc(II) does not react with 3,5-di-*t*-butylpyrocatechol in mildly alkaline solution but forms soluble hydroxo complexes in the pH range 7–8 with a single, steep inflection at $m = 2$. Apparently the monoanion of the ligand is too weak and the dianion too low in concentration to compete effectively with hydroxide for the metal ion. Pyrocatechol, on the other hand, being somewhat more acidic, reacts readily and completely forming an insoluble white complex.

The original interest in using manganese(II)–3,5-di-*t*-butylpyrocatechol as a model system for the autoxidation of pyrocatechols stemmed mainly from the reported high yield of relatively stable *o*-quinone monomer at room temperature,[40] suggesting that a single reaction pathway is being followed. The fact that complexation of the model system in mixed solvent is slow may be fortuitous in the sense that experiments can be designed which allow comparison between the efficiency of the free metal ion catalyzed and metal–ligand chelate autoxidation reactions. The exceptionally high stability found for manganese(II) chelates of catechols may be quite helpful in assisting metal ion mediated oxidation of the ligand.

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The Kinetics of the Reaction of Iron(III) Chelates of Aminopolycarboxylic Acids with Ascorbic Acid[1a]

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Abstract: The kinetics of the oxidation of ascorbic acid by the Fe(III) chelates of diethylenetriaminepentaacetic acid (DTPA), 1,2-cyclohexanediaminetetraacetic acid (CDTA), ethylenediaminetetraacetic acid (EDTA), and N-hydroxyethylethylenediaminetriacetic acid (HEDTA) have been investigated at 25 and 0.4°. In the pH range 1.8–3.45 the rates decrease in the sequence, Fe(III)–HEDTA > Fe(III)–EDTA > Fe(III)–CDTA > Fe(III)–DTPA. The differences in the rates of oxidation and the activation parameters of the oxidation reaction are discussed in terms of the charges on the oxidants.

There has been much interest recently in the study of ferric complexes as oxidants in electron-exchange reactions. The use of ferricyanide as an oxidant has been extensively reviewed by Thyagarajan.[2] The kinetics of the oxidation of Fe(II) ions by tris(1,10-phenanthroline)iron(III) ions and by a number of Fe(III) complexes of substituted 1,10-phenanthrolines, 2,2′-bipyridine, and 2,2′,2′′-terpyridine have been reported by Sutin and coworkers.[3] In these previous studies, the oxidants were ferric complexes which have delocalized electrons and possess reduction potentials higher than that of the aquo ion. Ferric complexes of aminopolycarboxylic acids, which possess reduction potentials lower than that of the aquo Fe(III) ion, have been generally neglected, with the exception of the Fe(III)–ethylenediaminetetraacetic complexes used by Grinstead[4] as an oxidant in the model peroxidase system for the oxidation of the salicylate ion.

The present investigation was undertaken to study the ferric chelates of aminopolycarboxylic acids as oxidants in kinetic studies on the oxidation of ascorbic acid. The present work is part of a general study of the catalytic effects of metal ions and metal chelates in oxidation reactions.

Experimental Section

Reagents. The L-ascorbic acid employed was Kodak White Label grade and was used without further purification. Samples of ethylenediaminetetraacetic acid (EDTA), N-hydroxyethylethylenediaminetriacetic acid (HEDTA), *trans*-1,2-diaminocyclohexanetetraacetic acid (CDTA), and diethylenetriaminepentaacetic acid (DTPA) were recrystallized from water and dried under vacuum. Purity of the various ligands was determined by potentiometric titration of dried samples, with and without the addition of excess calcium ion, with carbonate-free sodium hydroxide. Solutions of iron(III) nitrate, prepared from Fisher analytical grade materials, were standardized by titration with potassium permanganate and also by titration with EDTA,[5] with Tiron as the indicator. The results of the two methods agreed within the experimental error.

Potentiometric Measurements. The dissociation constants of L-ascorbic acid at 25 and 0.4° were determined by potentiometric titration in a medium of 0.10 M ionic strength containing potassium nitrate, with a Beckman Model G pH meter fitted with extension glass and calomel electrodes. The pH meter was calibrated in terms of hydrogen ion concentration with acetic acid buffer, as well as with standard HCl and NaOH. The data given by Harned and Owen[6] were used to calculate the hydrogen ion concentration in the presence of the buffer. The experimental solution of ascorbic acid was prepared from air-free distilled water, and an atmosphere of purified nitrogen was maintained in the titration cell to avoid any disturbing effects resulting from oxidation by molecular oxygen.

Kinetic Measurements. The pH value of the experimental solution was maintained constant during each run by a Beckman Model K automatic titrator fitted with extension glass and calomel electrodes. It was calibrated with acetic acid buffer and by titration of standard HCl and NaOH solutions. The ionic strength of

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