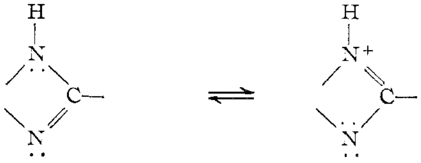
some of the derived metal chelate compounds. They characterized various bands for the first of these ligands in the 3, 5–7, and 7–15 μ spectral regions. In the 3 μ region the band at 3328 cm.$^{-1}$ attributed to the N–H stretching frequency dropped in frequency upon coordination with Ni(II), Co(II), and Zn(II) (see Table IV). This was attributed to the resonance structure on the right (below) making a greater contribution on coordination with a metal ion than before.



In the 5–7 μ region the band at 1664 cm.$^{-1}$ attributed to the C=N stretching frequency of the imidazoline ring dropped upon coordination. In the 7–15 μ region a peak at 996 cm.$^{-1}$ was assigned to the pyridine breathing mode. Coordination caused it to increase. This was explained as being due to the coordination bonding of the pyridine ring nitrogen atom to the metal ion, causing restriction in the breathing mode.

2-(2′-Pyridyl)imidazoline is a dihydro-2-(2′-pyridyl)imidazole with very similar structural features to those of I (R = H). Each compound may be regarded as a substituted 2-picolinamidine with practically identical structures in the donor nitrogen atoms section of the molecules. It is, therefore, not unreasonable to expect very similar infrared peaks in the spectral regions discussed above and similar shifts upon coordination. The observed frequencies are tabulated (Table IV). The observations were made in Nujol mulls using a Perkin-Elmer Model 221 spectrophotometer.

It is worth commenting that deprotonation of the cations of the complex salts giving neutral complexes strips each imidazole N–H group of its hydrogen. This is shown in the spectra by the disappearance of the N–H stretching peak in the 3 μ region. Replacement of this N–H by N–CH_3 (2-(2′-pyridyl)-1-methylimidazole) causes a similar disappearance of this band. Also, in the four silver complexes examined there is no change in frequency shown upon coordination in the pyridine breathing frequency, suggesting that the silver atom in these complexes is not bonded to the pyridine nitrogen atom.

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Contribution No. 1566 from the Department of Chemistry,
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Complexes of Chromium(II) and (III) with Ethylenediaminetetraacetic Acid[1]

By ROBERT L. PECSOK, L. DONALD SHIELDS,[2] and WILLIAM P. SCHAEFER

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A potentiometric and polarographic study of the Cr(II)-EDTA complex has yielded a value of 13.61 for log formation constant and 3.00 for minus log acidity constant. The log formation constant of the Cr(III)-EDTA complex is 23.40.

Introduction

In previous polarographic studies of chromium(II) in various complexing media,[3–5] we have noted that the Cr(II)–EDTA is a very powerful reductant with a half-wave potential of −1.48 v. *vs.* s.c.e. Its very fast reactions with oxygen, hydrogen ion, and/or hydroxide ion have made quantitative measurements very difficult. For example, although nearly all of the stability constants of the metal–EDTA complexes have been measured,[6] no values have yet been reported for either the Cr(II)–EDTA or the Cr(III)–EDTA complexes. With the results of this study, we now have a complete list of constants for divalent metal complexes of the first transition series.

Experimental

Reagents.—Chromium(II) chloride solutions were prepared from primary standard grade potassium dichromate as previously described[5] by reduction with hydrogen peroxide and a mercury cathode. The Cr(II) content was determined by indirect potentiometric titration with ceric solution after adding an excess of ferric ion. The Cr(III) content was determined spectrophotometrically and found to be less than 0.1% of the total Cr. Hydrogen ion was determined by potentiometric titration with sodium hydroxide.

Reagent grade disodium EDTA was assayed by titration with base. All solutions were finally adjusted to 0.1 *F* ionic strength with reagent grade potassium chloride.

pH Measurements.—We define pH as the negative logarithm of the hydrogen ion *concentration*. All pH measurements were made with a Radiometer PHM4C meter using a Radiometer G202B glass electrode. Solutions were adjusted to 0.100 *F* ionic strength at 20.00 ± 0.02°. The electrode was calibrated under the same conditions over the pH range 1 to 4, with a linear response of 58.20 mv./pH unit. Measurements were reproducible to ±0.2 mv.

Polarography.—The polarographic cell consisted of a thermostated beaker with an external saturated calomel electrode connected by a double compartment salt bridge filled with KCl solution. The cell resistance was 690 ohms. Polarograms were recorded on a Sargent XXI polarograph without damping. The slide wire was calibrated by checking the applied potential at two

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[2] du Pont Teaching Fellow, 1961–1962.

[3] R. L. Pecsok and J. J. Lingane, *J. Am. Chem. Soc.*, **72**, 189 (1950).

[4] R. L. Pecsok, *J. Chem. Educ.*, **29**, 597 (1952).

[5] R. L. Pecsok and W. P. Schaefer, *J. Am. Chem. Soc.*, **83**, 62 (1961).

[6] S. Chaberek and A. E. Martell, "Organic Sequestering Agents," John Wiley and Sons, New York, N. Y., 1959, p. 572.

points, during the first and last one-eighth of the wave, with a precision potentiometer. Half-wave potentials were determined with a reproducibility of ±1.0 mv. No maximum suppressors were used.

Results

pH Titrations of Cr(II)–EDTA Solutions.—Equimolar solutions of Cr(II) and EDTA were titrated with acid or base. In spite of extreme precautions to eliminate oxygen, it was not possible to prevent the oxidation of a significant amount of Cr(II) in the titration mixture. Apparently local excess of either acid or base is responsible for the extraneous oxidation. In order to circumvent this disturbing behavior, the titrations were simulated, point by point, by preparing mixtures of appropriate composition containing all species except the Cr(II) solution. The mixtures were thoroughly degassed with prepurified nitrogen and finally the Cr(II) solution was added. Such solutions came to equilibrium immediately and were stable for 15 min. before any oxidation could be detected. The data for a series of such solutions, varying in pH, are shown in Table I.

As a first approximation, it was assumed that the CrY^{-2} species is the dominant complex. Thus a number of equations can be set up as shown below.

$$C_M = [Cr^{+2}] + [CrY^{-2}] \tag{1}$$

$$C_Y = [CrY^{-2}] + [H_4Y] + [H_3Y^-] + [H_2Y^{-2}] \tag{2}$$

$$C_H = [H^+] + 4[H_4Y] + 3[H_3Y^-] + 2[H_2Y^{-2}] \tag{3}$$

where C_M, C_Y, and C_H represent the total formal concentrations of Cr(II), EDTA, and H^+, which are known quantities. In all solutions, $C_M = C_Y$.

Using the successive ionization constants of EDTA[7]: $k_1 = 1.009 \times 10^{-2}$, $k_2 = 2.128 \times 10^{-3}$, $k_3 = 6.902 \times 10^{-7}$, $k_4 = 5.470 \times 10^{-11}$, we can solve for $[H_2Y^{-2}]$ in terms of measured $[H^+]$ and known constants

$$[H_2Y^{-2}] = \{C_H - [H^+]\}/\beta \tag{4}$$

$$[Cr^{+2}] = [H_2Y^{-2}]\alpha \tag{5}$$

$$[CrY^{-2}] = C_M - [Cr^{+2}] \tag{6}$$

$$[Y^{-4}] = k_3k_4[H_2Y^{-2}]/[H^+]^2 \tag{7}$$

$$K_f = [Cr^{+2}][Y^{-4}]/[CrY^{-2}] \tag{8}$$

where K_f is the formation constant of the Cr(II)Y complex and

$$\alpha = \{[H^+]^2 + k_1[H^+] + k_1k_2\}/k_1k_2 \tag{9}$$

$$\beta = \{4[H^+]^2 + 3k_1[H^+] + 2k_1k_2\}/k_1k_2 \tag{10}$$

$$\bar{n} = [CrY^{-2}]/C_M \tag{11}$$

The data from Table I provide a range of $\bar{n}$ from 0.406 to 0.885. Calculations of log K_f following the above treatment gave values varying from 13.68 to 13.04; *i.e.*, a definite trend with pH. Clearly a second complex is indicated, $CrHY^-$. We define the acidity constant of this complex

$$K^H = [H^+][CrY^{-2}]/[CrHY^-] \tag{12}$$

An additional term, $[CrHY^-]$, must now be added to eq. 1–3, and corresponding changes made in eq. 4–6 and 11. Since the value of K^H is unknown, a unique solution of these equations is not possible. For example, solving for $[H_2Y^{-2}]$

$$[H_2Y^{-2}] = \frac{C_H - C_Y + K^HC_H/[H^+] - K^H - [H^+]}{\beta K^H/[H^+] + \beta - \alpha} \tag{13}$$

Assumed values for pK^H over the range 2.65 to 4.00 were used to solve for log K_f. A plot of log K_f *vs.* pK^H for each mixture in Table I gives a family of curves all of which intersect at a common point. Selected but critical results are shown in Table I. The validity of this treatment and the accuracy of the constants is indicated by the very small spread in the values of log K_f for pK^H = 3.000.

TABLE I

DATA AND CALCULATIONS FOR Cr(II)–EDTA SOLUTIONS

$C_M = C_Y \times 10^3$ *F*	$C_H \times 10^3$ *F*	pH	$\bar{n}$	log K_f $-\infty^a$	log K_f 2.750^a	log K_f 3.000^a	log K_f 3.250^a
3.406	0.950	3.851	0.885	13.04	13.31	13.60	14.51
3.406	1.200	3.732	0.857	13.09	13.36	13.63	14.46
3.406	1.450	3.639	0.829	13.11	13.37	13.62	14.34
3.406	2.690	3.321	0.704	13.24	13.44	13.61	13.94
3.121	4.365	3.016	0.539	13.48	13.55	13.60	13.66
3.121	4.675	2.975	0.514	13.51	13.57	13.60	13.63
3.121	5.045	2.930	0.488	13.55	13.59	13.60	13.60
3.121	5.305	2.893	0.473	13.60	13.61	13.61	13.60
3.121	5.615	2.858	0.453	13.63	13.64	13.63	13.59
3.121	6.300	2.793	0.406	13.68	13.64	13.60	13.53

[a] Column headings are assumed values for pK^H. $-\infty$ is for $K^H = \infty$; *i.e.*, ($CrHY^-$) assumed to be zero.

Magnetic Measurements.—Magnetic susceptibility measurements with the Gouy balance technique yield a magnetic moment of 5.12 B.M. for the CrY^{-2} complex, compared to a theoretical value of 4.90 B.M. for a d^4 high-spin configuration.

Polarography.—All solutions polarographed contained a small amount of Cr(III) due to unavoidable oxidation. The composite wave obtained had no inflection at zero current. The difference, $E_{3/4} - E_{1/4}$, was 55.5 ± 1.0 mv., compared to a theoretical value of 55.4 mv. for a reversible one-electron oxidation at 20.0°. The current was diffusion controlled over the pH range studied (pH 4–6) and the total anodic plus cathodic current was independent of the ratio of Cr(II)/Cr(III). Thus the diffusion current constant for both CrY^{-2} and CrY^- is 1.46 ± 0.02 at 20°, $\mu = 0.1$.

The half-wave potential is independent of the concentration of both Cr(II) and EDTA. Well-defined waves were obtained over a wide range of pH. Below pH 4, the reduction of hydrogen ion interferes with the Cr(II), although the half-wave potential appears to become more positive with decreasing pH in this region. The dependence of half-wave potential on pH is shown in Table II.

The half-wave potential is independent of pH in the range 4–6 and then becomes more negative by 50.7 mv./pH unit in the range 8–10. Above pH 11, the wave tends toward irreversibility and becomes independent of pH with a half-wave potential of −1.48 v.

The polarographic behavior can be interpreted in agreement with the titration data above for the Cr-

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(7) G. Schwarzenbach and H. Ackermann, *Helv. Chim. Acta*, **30**, 1798 (1947).

TABLE II

HALF-WAVE POTENTIAL OF THE Cr(II)–EDTA COMPLEX

[Cr(II)] = 6.02 × 10^{-4} *F*, [EDTA] = 3.90 × 10^{-2} *F*, [KCl] = *ca.* 0.1 *F*

pH	$-E_{1/2}$, v. *vs.* s.c.e.	pH	$-E_{1/2}$, v. *vs.* s.c.e.
4.140	1.244	6.717	1.234
4.360	1.226	7.025	1.235
5.062	1.227	7.370	1.240
5.340	1.227	8.042	1.270
5.504	1.227	9.041	1.318
5.716	1.226		
6.026	1.230	9.620	1.349
6.312	1.231	10.052	1.372

(II)–EDTA system and the spectrophotometeric data for the Cr(III)–EDTA system.[8] The electrode reactions proposed for the various pH ranges are

$$\text{pH} < 4;\ \text{Cr(HY)(H}_2\text{O)}^- = \text{CrY(H}_2\text{O)}^- + \text{H}^+ + \text{e}$$

$$\text{pH 4–6};\ \text{CrY(H}_2\text{O)}^{-2} = \text{CrY(H}_2\text{O)}^- + \text{e}$$

$$\text{pH 8–10};\ \text{CrY(H}_2\text{O)}^{-2} = \text{CrY(OH)}^{-2} + \text{H}^+ + \text{e}$$

$$\text{pH} > 11;\ \text{CrY(OH)}^{-3} = \text{CrY(OH)}^{-2} + \text{e}$$

From the half-wave potential in the pH range 4–6, where the total ionic strength was adjusted to 0.1 *F*, and the previously determined formation constant of the Cr(II)–EDTA complex, the formation constant of the Cr(III)–EDTA complex can be calculated in the usual way.[9] Unfortunately the half-wave potential of the Cr(II)/Cr(III) couple in noncomplexing media includes a substantial overvoltage. Therefore the value determined by Grube and Breitinger[10] was used, $E^0 = -0.412$ v. *vs.* n.h.e. at 19°. The value obtained, $\log K_f = 23.40$, is in line with earlier predictions.

Discussion

With this report, we can now list the formation and acidity constants of all divalent metal–EDTA complexes of the first transition series. In Table III, these values are compared with the sum of the first and second ionization potentials of the metals.

TABLE III

FORMATION AND ACIDITY CONSTANTS OF EDTA COMPLEXES OF FIRST TRANSITION SERIES

Temperature = 20°, μ = 0.1 *F*

Metal	$\log K_f$	pK^H	E_2[a]	$E_1 + E_2$[b]
V(II)	12.70	3.5	338	493
Cr(II)	13.61	3.00	380	536
Mn(II)	13.58	3.1	361	532
Fe(II)	14.33	2.8	373	554
Co(II)	16.31	3.0	393	574
Ni(II)	18.56	3.2	418	594
Cu(II)	18.79	3.0	468	646
Zn(II)	16.26	3.0	414	631

[a] Second ionization potential, kcal./mole. [b] First plus second ionization potentials, kcal./mole.

The stabilization of the Cr(II) complex by the ligand field effect makes the Cr(II) more stable than the Mn(II) complex, although this effect is not as extreme as for the Ni(II) and Cu(II) complexes when compared to the Zn(II) complex with its d^{10} configuration. As is the case with the other complexes of this group (except for V(II)) the pK^H is within the range 3.0 ± 0.2. Following Higginson's argument,[11] we propose a quinquedentate structure for the Cr(II)–EDTA complex, in a distorted octahedron with a water molecule occupying the less stable d_{z^2} position.

Acknowledgment.—The magnetic measurements reported herein were made by Mr. R. Garber.

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[8] C. Furlani, G. Morpurgo, and G. Satori, *Z. anorg. allgem. Chem.*, **303**, 1 (1960).

[9] I. M. Kolthoff and J. J. Lingane, "Polarography," 2nd Ed., Interscience Publishers, New York, N. Y., 1952.

[10] G. Grube and A. Breitinger, *Z. Elektrochem. angew. physik. Chem.* **33**, 112 (1927).

[11] W. C. E. Higginson, *J. Chem. Soc.*, 2761 (1962).

CONTRIBUTION FROM THE MELLON INSTITUTE
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Metal Nitrosyls. I. Triphenylphosphine Nitrosyl Nickel Complexes[1]

BY ROBERT D. FELTHAM

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The preparation and properties of some stable nitrosyl nickel complexes of the type $NiXNOL_2$ are reported. Several new methods for preparing these compounds are also discussed.

Methods for preparing nitrosyl nickel compounds have been known for quite a long time,[2-4] but the composition of the materials obtained from these reactions was uncertain. This uncertainty was due to the reactivity of the compounds formed in these reactions. With the exception of nitrosylcyclopentadienylnickel,[5] the first relatively stable compound, $NiBrNO[(C_6H_5)_3P]_2$, has only been briefly described.[6] Subse-

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[1] This research was sponsored by The International Nickel Company, Inc.

[2] R. L. Mond and A. E. Wallis, *J. Chem. Soc.*, **121**, 32 (1922).

[3] H. Reihlen, A. Gruhl, G. von Hessling, and O. Pfrengle, *Liebigs Ann.*, **482**, 161 (1930).

[4] J. S. Anderson, *Z. anorg. allgem. Chem.*, **229**, 357 (1936).

[5] T. S. Piper, F. A. Cotton, and G. Wilkinson, *J. Inorg. Nucl. Chem.*, **1**, 165 (1955).

[6] R. D. Feltham, *ibid.* **14**, 307 (1960).