System.—Following the method of Bjerrum[6] in which measurements of the pH of solutions of metal ions and complexing agents may be interpreted to give information concerning the formulas and stability constants of the complexes formed in the system, we find that two complexes are formed between chromium(II) and acetylacetone and have obtained values for the formation constants β_1 and β_2, where

$$\beta_n = \frac{[\mathrm{Cr(acac)}_n{}^{+2-n}]}{[\mathrm{Cr}^{+2}][\mathrm{acac}^-]^n}$$

We assume complexation and ionization reactions in this system to be as follows.

$$\mathrm{Cr}^{+2} + \mathrm{Hacac} \rightleftharpoons \mathrm{Cr(acac)}^+ + \mathrm{H}^+$$
$$\mathrm{Cr(acac)}^+ + \mathrm{Hacac} \rightleftharpoons \mathrm{Cr(acac)}_2 + \mathrm{H}^+$$
$$\mathrm{Hacac} \overset{K_1}{\rightleftharpoons} \mathrm{acac}^- + \mathrm{H}^+$$

In an earlier paper,[4] a similar system has been discussed. Proceeding in an analogous way for this system, we obtain for the average number of ligands bound ($\bar{n}$) per metal ion the expression

$$\bar{n} = \frac{K_1 + [\mathrm{H}^+]}{[\mathrm{H}^+]\Sigma_{\mathrm{Cr}}}\left\{[\mathrm{H}^+] + 2\Sigma_{\mathrm{Cr}} + [\mathrm{K}^+] + [\mathrm{Na}^+] - \frac{K_{\mathrm{w}}}{[\mathrm{H}^+]} - [\mathrm{Cl}^-] - \Sigma_{\mathrm{acac}}\left(\frac{K_1}{K_1 + [\mathrm{H}^+]}\right)\right\}$$

where Σ_{Cr} is the total concentration of Cr(II) and Σ_{acac} is the total concentration of acetylacetone.

Solutions containing chromous chloride and hydrochloric acid were titrated to obtain the formation function of the system. Several attempts were made to form the complex in basic solution, then to titrate the excess base and the complex with standard acid, in this way approaching the equilibrium from the opposite direction. The results were unsatisfactory in that obviously rapid oxidation of the chromous ion occurred in the basic solution, as evidenced by the formation of the violet color of chromic ion.

With all quantities on the right-hand side of the equation easily calculated and the hydrogen ion concentration readily measured, it is possible to calculate $\bar{n}$ and to plot the results *vs.* p[acac]. From this plot the formation constants for the system were obtained using the "correction-term" method of Irving and Rossotti.[7]

This method assumes the formation function is symmetric about $\bar{n} = 1$. The formation curves obtained from many of the titrations were distorted and could not be analyzed in this manner. This was probably due to the oxidation of some of the chromous ion during the titration, as the solutions that gave suspect formation curves were always discolored. Two titrations gave quite symmetric curves from which the successive formation constants of the system could be calculated as $\log \beta_1 = 5.96 \pm 0.02$ and $\log \beta_2 = 11.70 \pm 0.03$. These formation constants were used to calculate a theoretical formation function for the chromium(II)–acetylacetone system and the calculated values are compared with the experimental values in Table II.

Attempts were made to measure the reduction potential of the chromium(II)–acetylacetone complex by direct potentiometry and by polarography. Direct measurements of the potential of a platinum electrode in solutions containing the complex gave wildly erratic results; these are ascribed to the reduction of hydrogen ion at the electrode by the complex. In one instance, bubbles of gas appeared on a clean electrode after a few minutes. Solutions of the complex in near-neutral media do not give polarographic waves at the dropping mercury electrode. Therefore, we can only agree that the complex is a powerful reducing agent, as has previously been stated.[2]

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(6) J. Bjerrum, "Metal Ammine Formation in Aqueous Solution," P. Haase and Sons, Copenhagen, 1941.

(7) H. Irving and H. S. Rossotti, *J. Chem. Soc.*, 3397 (1953).

Correspondence

Five-Coordinate Intermediates in the Base Hydrolysis of Cobalt(III) Complexes[1]

Sir:

The base hydrolysis of complexes of the type $[\mathrm{Co(en)_2AX}]^{n+}$, where en = ethylenediamine, A = OH, Cl, Br, N_3, NCS, NH_3, NO_2, and X = Cl, Br, NO_3, NCS, N_3, have been extensively investigated by Ingold, Nyholm, Tobe, and co-workers,[2] and while their results have been rationalized in terms of an SN2 mechanism involving OH^- attack at the cobalt, the rate law for the reactions is not inconsistent with an SN1CB mechanism.[3] Moreover, the recent isotopic fractionation experiments by Green and Taube[4] on the base hydrolysis of the $[\mathrm{Co(NH_3)_5X}]^{2+}$ system (where X = Cl, Br, NO_3) suggest that this reaction occurs *via* a common intermediate. The result also implies that the observations of Tobe, *et al.*, could be consistent with the production of a five-coordinate intermediate and is particularly relevant when one considers the production of a common intermediate from several different sources, *i.e.*, where the reference group A remains constant and the leaving group varies. Under these circumstances the concentrations of the isomeric products should be independent of the group departed for a particular inter-

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(1) This work was supported by the A.E.C. under contract No. AEC AT(04-3)-326.

(2) D. D. Brown, C. K. Ingold, and R. S. Nyholm, *J. Chem. Soc.*, 2674 (1953); D. D. Brown and C. K. Ingold, *ibid.*, 2680 (1953); C. K. Ingold, Weizmann Memorial Lecture, 1958; M. L. Tobe, *Sci. Progr.*, **48**, 483 (1960).

(3) (a) F. J. Garrick, *Nature*, **139**, 507 (1937); (b) F. Basolo and R. G. Pearson, "Mechanism of Inorganic Reactions," John Wiley and Sons, New York, N. Y., 1958, p. 124; (c) F. Basolo and R. G. Pearson, *Advan. Inorg. Chem. Radiochem.*, **3**, 25 (1960).

(4) M. Green and H. Taube, *Inorg. Chem.*, **2**, 948 (1963).

TABLE I
PRODUCTS OF THE BASE HYDROLYSIS OF *cis*-AND *trans*-$[Co(en)_2AX]^{n+}$

Reactant		Product	% *cis*	Ref.
trans-$[Co(en)_2ClBr]^+$	→	$[Co(en)_2ClOH]^+$	5 (±5)[a]	*c*
trans-$[Co(en)_2ClCl]^+$	→	$[Co(en)_2ClOH]^+$	5 (±2)	*c*
trans-$[Co(en)_2N_3NCS]^+$	→	$[Co(en)_2NCSOH]^+$	70	*d*
trans-$[Co(en)_2ClNCS]^+$	→	$[Co(en)_2NCSOH]^+$	76	*e*
trans-$[Co(en)_2BrNCS]^+$	→	$[Co(en)_2NCSOH]^+$	81 (±3)	*e*
trans-$[Co(en)_2BrOH]^+$	→	$[Co(en)_2OHOH]^+$	90 (±2)	*c*
trans-$[Co(en)_2ClOH]^+$	→	$[Co(en)_2OHOH]^+$	94 (±2)	*c*
trans-$[Co(en)_2ClNO_2]^+$	→	$[Co(en)_2NO_2OH]^+$	6 (±3)	*f*
trans-$[Co(en)_2NCSNO_2]^+$	→	$[Co(en)_2NO_2OH]^+$	10	*g*
trans-$[Co(en)_2N_3Cl]^+$	→	$[Co(en)_2N_3OH]^+$	27[b] (13)	*h*
trans-$[Co(en)_2N_3N_3]^+$	→	$[Co(en)_2N_3OH]^+$	30 (±5)	*h*
trans-$[Co(en)_2N_3NCS]^+$	→	$[Co(en)_2N_3OH]^+$	60??	*d*
cis-$[Co(en)_2ClBr]^+$	→	$[Co(en)_2ClOH]^+$	30 (±5)	*c*
cis-$[Co(en)_2ClCl]^+$	→	$[Co(en)_2ClOH]^+$	37 (±2)	*c*
cis-$[Co(en)_2ClNO_2]^+$	→	$[Co(en)_2NO_2OH]^+$	67 (±7)	*f*
cis-$[Co(en)_2NCSNO_2]^+$	→	$[Co(en)_2NO_2OH]^+$	55	*g*
cis-$[Co(en)_2ClNH_3]^{+2}$	→	$[Co(en)_2NH_3OH]^{+2}$	84	*i*
cis-$[Co(en)_2BrNH_3]^{+2}$	→	$[Co(en)_2NH_3OH]^{+2}$	85	*i*
cis-$[Co(en)_2NO_3NH_3]^{+2}$	→	$[Co(en)_2NH_3OH]^{+2}$	86	*i*
cis-$[Co(en)_2ClOH]^+$	→	$[Co(en)_2OHOH]^+$	97 (±2)	*c*
cis-$[Co(en)_2BrOH]^+$	→	$[Co(en)_2OHOH]^+$	96 (±2)	*c*
cis-$[Co(en)_2N_3Cl]^+$	→	$[Co(en)_2N_3OH]^+$	59[b] (51)	*h*
cis-$[Co(en)_2N_3N_3]^+$	→	$[Co(en)_2N_3OH]^+$	55 (±5)	*h*
cis-$[Co(en)_2N_3NCS]^+$	→	$[Co(en)_2N_3OH]^+$	100??	*d*
cis-$[Co(en)_2NCSCl]^+$	→	$[Co(en)_2NCSOH]^+$	80	*h, i*
cis-$[Co(en)_2NCSN_3]^+$	→	$[Co(en)_2NCSOH]^+$	70	*d*

[a] The values in parentheses are from the original reference. [b] Values recalculated using ϵ 110 for *trans*-$[Co(en)_2N_3OH_2]^{+2}$ (D. A. Loeliger and H. Taube, to be published). [c] S. C. Chan and M. L. Tobe, *J. Chem. Soc.*, 4531 (1962). [d] P. J. Staples, *ibid.*, 3227 (1963). [e] C. K. Ingold, R. S. Nyholm, and M. L. Tobe, *ibid.*, 1691 (1956). [f] S. Asperger and C. K. Ingold, *ibid.*, 2862 (1956). [g] A. Roger and P. J. Staples, *ibid.*, 4749 (1963). [h] P. J. Staples and M. L. Tobe, *ibid.*, 4803 (1960). [i] R. S. Nyholm and M. L. Tobe, *ibid.*, 1707 (1956).

mediate although they could vary from one type of intermediate to the next.[3c]

In this context the data in Table I are arranged to show the remarkable agreement between the concentrations of isomeric products from different parents where a common intermediate is conceived for the SN1CB mechanism.

Some comment is needed on the accuracy of the numbers in Table I, particularly for the reactions *cis*- and *trans*-$[Co(en)_2N_3NCS]^+ \rightarrow [Co(en)_2N_3OH]^{2+}$. In both instances the method of analysis of the complex mixture is insensitive to the product composition and these apparent exceptions may well conform to the general agreement above. The same comment is true, although to a lesser extent, for the product analysis from *cis*- and *trans*-$[Co(en)_2N_3NCS]^+ \rightarrow [Co(en)_2NCSOH]^+$ and *cis*-$[Co(en)_2NCSNO_2]^+ \rightarrow [Co(en)_2NO_2OH]^+$. In addition the product composition for the reactions *cis*- and *trans*-$[Co(en)_2ClN_3]^+ \rightarrow [Co(en)_2N_3OH]^+$ was redetermined using the extinction coefficient (110) for *trans*-$[Co(en)_2N_3OH_2]^{2+}$ obtained by Loeliger and Taube,[5] and the recalculated values are in better agreement with the products from *trans*-$[Co(en)_2(N_3)_2]^+$ than formerly.

This communication was prompted by some recent studies on the catalyzed aquation of some of the bis(ethylenediamine) disubstituted cobalt(III) complexes[5,6] where the same stereochemical products were obtained from different sources and a common intermediate was proposed. So far the stereochemical results for base hydrolysis also are consistent with the production of a five-coordinate intermediate; it will now be interesting to see what effect the temperature has on the product distribution and also if the correlation holds over a wider range of leaving groups.

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(5) D. A. Loeliger and H. Taube, to be published.

(6) A. M. Sargeson, *Australian. J. Chem.*, **17**, 385 (1964).

A Simple Molecular Orbital Description of the Charge-Transfer Spectra of Some Substituted Borazines

Sir:

From a study of π-complexes, Muzskat and Kirson[1] have inferred the following order of ionization potentials: 1,3,5-$(C_6H_5)_3C_6H_3 < (C_6H_5NBH)_3 < (C_6H_5BNH)_3$. In addition, the relative ionization potentials, $(C_6H_5NBCH_3)_3 < (C_6H_5BNCH_3)_3$, probably holds because the latter compound in the presence of tetracyanoethylene does not display a visible charge-transfer band while the former does.[1] Muzskat and Kirson employed a variety of steric, inductive, and resonance arguments to explain the observed orders. Our previous success in the correlation of reduction potentials of phenyl-substituted borazines with Hückel molecular orbital calculations[2] led us to apply a similar treatment to the present problem.

Within the framework of simple MO theory the ionization potential is equal to the energy of the highest filled π-molecular orbital; this energy is easily calculated, providing sufficient information is available to establish values for the Coulomb and resonance integrals. In the present calculations we employed parameters h_B, h_N, and k_{BN} which had been used to fit reduction potentials of phenylborazines.[2] In addition, k_{CB} (inter-ring) and k_{CN} (inter-ring) were varied by cos θ,[3] where the twist angle (θ) was assigned a variety of values which encompass our previous estimate of 20°, based on analogy with biphenyl, and also Muzskat and Kirson's estimates, based on molecular models. As these authors have pointed out the choice of θ is not highly critical for qualitative discussions of relative energies. The problem of how to include methyl substituent effects on borazine has not been investigated by Hückel MO methods. However, Kaufman and Hamann have presented arguments in favor of employing methyl substituent parameters determined for hy-

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(1) K. A. Muzskat and B. Kirson, *Israel J. Chem.*, **2**, 57 (1964).

(2) D. F. Shriver, D. E. Smith, and P. Smith, *J. Am. Chem. Soc.*, **86**, 5153 (1964).

(3) The extent of overlap is proportional to cos θ. In their use of $\cos^2 \theta$ Muzskat and Kirson appear to misinterpret a paper by Dewar [*J. Am. Chem. Soc.*, **74**, 3345 (1952)] in which it is shown that the resonance energy is proportional to $\cos^2 \theta$ for certain conjugated systems. The resonance energy is determined from the total π energy of a conjugated system and is not pertinent to a discussion of ionization potentials, which depend on the energy of a single level.