rate of the chemical reaction to be greatly enhanced by the addition to the MeCN solution of small amounts of a strong proton donor such as phenol. It seems likely, then, that the proton-assisted reaction (3) may be resulting in protonation at the *metal* rather than at the ligand, although we have not yet obtained direct evidence to support this hypothesis. In view of the expected highly basic character of the metal in Cp_2Co^-, such a reaction would not seem anomalous and would signal the investigation of a series of reactions between electrophiles and the Co(I) atom.

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Reactions of Coordinated Nucleophiles. Intramolecular Imine Formation

Sir:

The facility with which coordinated nucleophiles can attack reactive centers within a metal complex has been suspected for a long time. Usually the complexes have been too labile for the assertion to be proved although a few examples are known[1] where neither the coordinated nucleophile nor the ligand which is attacked actually ever leave the metal ion. Processes of this kind are commonly assumed to be involved in so-called "metal template" synthesis[2] though unequivocal proof that the reaction does occur while the reactants are fully coordinated appears to be lacking. A common and important process in "template" syntheses is the formation of the carbon–nitrogen double bond (imine), and we are currently investigating several kinetically inert complexes wherein this is observed as a rapid-intramolecular process. This is part of a program designed to evaluate the efficiency and potentiality of such intramolecular reactions, and we describe here such a condensation.

When the pH of a dilute[3] aqueous solution of pyruvatopentaamminecobalt(III) ion, $[(NH_3)_5CoO_2C\text{-}COCH_3]^{2+}$ (A), was raised to ≥ 12, an intense brown-red color rapidly developed. Acidification with $HClO_4$ immediately produced a clear orange solution from which a crystalline perchlorate salt was isolated. Dissolution of this solid in aqueous NaOH (0.05 *M*)

(1) (a) D. A. Buckingham, D. M. Foster, and A. M. Sargeson, *J. Amer. Chem. Soc.*, 91, 3451 (1969); (b) *ibid.*, 91, 4102 (1969); (c) D. A. Buckingham, D. M. Foster, L. G. Marzilli, and A. M. Sargeson, *Inorg. Chem.*, 9, 11 (1970); (d) D. A. Buckingham, D. M. Foster, and A. M. Sargeson, *J. Amer. Chem. Soc.*, 92, 6151 (1970); (e) D. A. Buckingham, C. E. Davis, and A. M. Sargeson, *ibid.*, 92, 6159 (1970).

(2) For reviews of this extensive area of chemistry see N. F. Curtis *Coord. Chem. Rev.*, 3, 3 (1968); D. H. Busch, K. Farmery, V. Goedken, V. Katovic, A. C. Melnyk, C. R. Sperati, and N. Tokel, *Advan. Chem. Ser.*, No. 100, 44 (1971); L. F. Lindoy and D. H. Busch "Preparative Inorganic Reactions," Vol. 6, W. L. Jolly, Ed., Interscience, New York, N. Y., 1971, p 1.

(3) In concentrated solutions another reaction, leading to polymeric complex products, is observed. While of interest, this reaction is not relevant to the present report and may readily be made insignificant by appropriate choice of conditions.
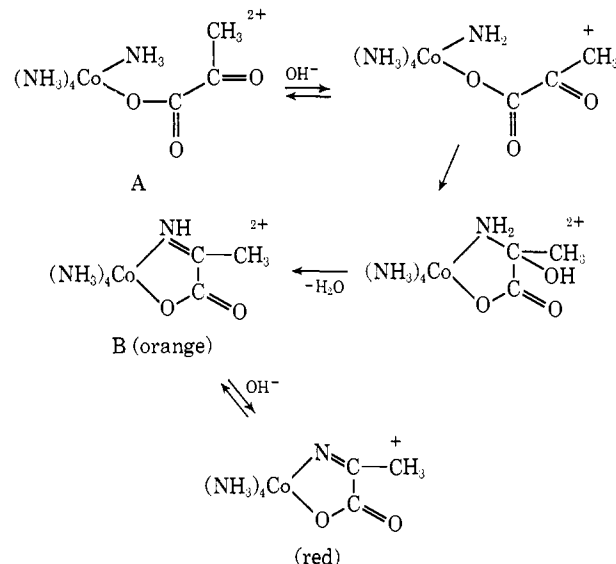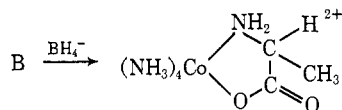
immediately regenerated the intense red color indicating it was simply due to a product deprotonation reaction ($pK_a = 10.5$ at 25°, $\mu = 1.0$, $NaClO_4$). The red species slowly decomposed in the basic medium. At lower pH (≈ 10) the reaction proceeded more slowly (~ 5 min) and directly to the orange product which appeared to be indefinitely stable in quite concentrated acid (3 *M* HCl). Analysis of the perchlorate salt was consistent with loss of 1 mol of water from the reactant. *Anal.* Calcd for $CoC_3H_{16}N_5O_{10}Cl_2$: Co, 14.30; C, 8.75; H, 3.91; N, 17.00; Cl, 17.21. Found: Co, 14.48; C, 8.81; H, 4.08; N, 16.75; Cl, 16.84. Infrared and pmr spectra provide convincing evidence that the orange product is the pyruvilidene–imine chelate complex of tetraamminecobalt(III) (B). Thus, the process results in replacement of the $>C=O$ stretching absorption at 1720 cm^{-1} in the reactant by a strong product band at 1680 cm^{-1} ($\nu_{C=N}$), just resolved from carboxylate absorption (in the N-deuterated complexes). In DMSO-d_6 proton magnetic resonances appear at δ (ppm) -12.1 ($=NH$), -3.92 (NH_3), -3.33 (2 NH_3), -2.94 (NH_3), and -2.36 ($N=CCH_3$) relative to internal tetramethylsilane. The reaction is assumed to occur by attack of the deprotonated ammonia cis to the carboxylate ligand at the carbonyl center of the keto form of coordinated pyruvate although it is known that the gem-diol form is present in significant amounts.[4] Preliminary kinetic measurements indicate that the carbinolamine intermediate does not attain significant concentrations, the reaction appearing as a single rate process first order in reactant complex concentration. The dependence of the rate on hydroxide ion concentration is not simple, being close to first order between pH 8 and 11, but declining to zero order for $[OH^-] \gtrsim 0.5$ *M*. In 1 *M* NaOH the half-life of reaction is ~ 0.2 sec at 25°. At lower pH values proton exchange at the ammonias cis to the pyruvate ligand exceeds the reaction rate by a factor $\sim 2 \times 10^2$ only. Clearly the coordinated amide ion is fairly efficient at capturing the $>C=O$ center. The specific rate of chelation of the deprotonated reactant is estimated at $\gtrsim 7000$ sec^{-1} at 25° using the esti-
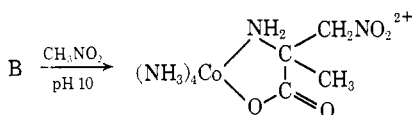
(4) (a) H. J. Price and H. Taube, *J. Amer. Chem. Soc.*, 89, 269 (1967); (b) *Inorg. Chem.*, 7, 1 (1968); (c) L. Pratt and G. Occupati, *J. Chem. Soc., Dalton Trans.*, 1699 (1973).

mated value of 16 for the pK_a of coordinated NH_3 at Co(III).[5]

Several reactions characteristic of imines[6] support the proposal for the pyruvilidene–imine structure. Reduction with BH_4^- ion rapidly generates alaninatotetra-amminecobalt(III) ion, subsequently isolated as its chloride salt and with properties characteristic of this species. *Anal.* Calcd for $CoC_3H_{18}N_5O_2Cl_2$: Co,

$$B \xrightarrow{BH_4^-} (NH_3)_4Co \underset{O}{\overset{NH_2}{<}} \underset{C}{\overset{C}{\underset{O}{\diagdown}}} \overset{H}{\underset{CH_3}{C}} \quad {}^{2+}$$

20.60; C, 12.60; H, 6.34; N, 24.48; Cl, 24.79. Found: Co, 20.90; C, 12.62; H, 6.29; N, 23.96; Cl, 24.64. Pmr spectroscopy after deuteration of the N centers showed a doublet centered at δ -1.49 ppm ($CHCH_3$) and a quartet centered at δ -3.73 ppm ($CHCH_3$). Michael addition of carbanions occurred rapidly. For example nitromethane in aqueous Na_2CO_3 buffer (pH 10) gave

$$B \xrightarrow[pH\ 10]{CH_3NO_2} (NH_3)_4Co \underset{O}{\overset{NH_2}{<}} \underset{C}{\overset{C}{\underset{O}{\diagdown}}} \overset{CH_2NO_2}{\underset{CH_3}{C}} \quad {}^{2+}$$

isolated as the perchlorate salt. *Anal.* Calcd for $CoC_4H_{19}N_6O_{12}Cl_2$: Co, 12.46; C, 10.16; H, 4.05; N, 17.76; Cl, 14.99. Found: Co, 12.59; C, 10.53; H, 4.22; N, 17.70; Cl, 15.05.

It is clear that reactions of this type have great potential for building chelates, both imine and saturated amine chelates, and the application of the process for this purpose and for stereospecific isomer synthesis will be demonstrated later.

(5) D. A. Buckingham, L. G. Marzilli, and A. M. Sargeson, *J. Amer. Chem. Soc.*, **89**, 3428 (1967).
(6) S. Patai, Ed., "The Chemistry of the Carbon-Nitrogen Double Bond," Interscience New York, N. Y., 1970.

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Structural Trans Effect in Sulfur Bound Sulfitopentaamminecobalt(III) Chloride Monohydrate

Sir:

We have recently shown[1] a small (0.04 Å) but significant sulfur structural trans effect in cobalt(III) complexes with thiolato ligands. Sulfur bound, dimethyl sulfoxide has been found[2] to exert a comparable effect in a ruthenium(II) complex. The sulfur bound sulfito-pentaamminecobalt(III) cation has been shown to possess an extremely large *kinetic* trans effect.[3] Since an X-ray structure determination[4] for *trans*-Co(en)₂-SO₃NCS shows no significant lengthening of the cobalt–thiocyanate bond, the kinetic effect has been ascribed[5]

(1) R. C. Elder, L. R. Florian, R. E. Lake and A. M. Yacynych, *Inorg. Chem.*, **12**, 2690 (1973).
(2) F. C. March and G. Ferguson, *Can. J. Chem.*, **49**, 3590 (1971).
(3) J. Halpern, R. A. Palmer, and L. M. Blakely, *J. Amer. Chem. Soc.*, **88**, 2877 (1966).
(4) S. Baggio and L. N. Becka, *Acta Crystallogr., Sect. B*, **25**, 946 (1969).
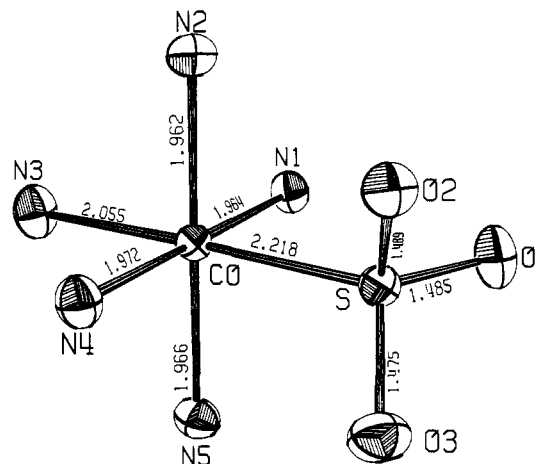
Figure 1. A perspective view of $[(NH_3)_5CoSO_3]^+$. The ellipsoids represent 50% probability.

to a stabilization of the transition state of the substitution reaction. We have determined the structure of sulfur bound sulfitopentaamminecobalt(III) chloride monohydrate, $[(NH_3)_5CoSO_3]Cl \cdot H_2O$, and found a large structural trans effect in this compound.

A sample of sulfitopentaamminecobalt(III) sulfite, $[(NH_3)_5CoSO_3]_2SO_3$, was supplied by Professor J. Halpern of the University of Chicago and was converted to the monohydrate chloride salt, $[(NH_3)_5CoSO_3]$-$Cl \cdot H_2O$, by known procedures.[6] This compound crystallizes in the monoclinic system with the following unit cell constants: $a = 12.142\ (2)$, $b = 6.664\ (3)$, $c = 12.317\ (2)$ Å; $\beta = 95.77\ (2)°$; space group $P2_1/c$ No. 14,[7] $Z = 4$; $d_{calcd} = 1.87$, $d_{measd} = 1.87\ (2)$ g cm⁻³. The structure was solved by standard Patterson techniques. Least-squares refinement using anisotropic thermal parameters for all nonhydrogen atoms and isotropic temperature parameters for hydrogen atoms gives a current value of the conventional R factor[8] of 0.028 and a weighted R factor[9] of 0.032. The 1979 unique reflections used for refinement were measured with a Syntex $P\bar{1}$ diffractometer.

The structure of the complex cation is shown in Figure 1, which also lists the bond lengths. The average Co–N distance for those ammonia ligands cis to sulfur is 1.966 (4) Å, whereas the trans Co–N length is 2.055 (2) Å. The difference between cis and trans distances is thus 0.089 (4) Å showing a comparatively large sulfur structural trans effect. Thus, there is a significant lengthening of the trans cobalt–nitrogen bond in the ground state of the complex and the large kinetic trans effect observed for the aquation of $[(NH_3)_5$-$CoSO_3]^+$ must result at least partially from a ground-state weakening of the trans cobalt–nitrogen bond. Further studies of the sulfur structural trans effect are in progress and will be reported subsequently.

(5) J. F. Byrd and W. K. Wilmarth, *Inorg. Chim. Acta, Rev.*, **5**, 7 (1971).
(6) A. Werner and Von H. Grüger, *Z. Anorg. Chem.*, **16**, 398 (1898).
(7) "International Tables for X-Ray Crystallography," Vol. 1, 2nd ed, Kynoch Press, Birmingham, England, 1965.
(8) $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$.
(9) $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w(F_o)^2]^{1/2}$.

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