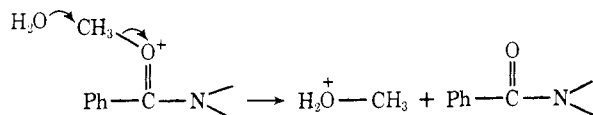activation[4] and positive "*r*" hydration parameters[7] previously observed, it appears to be a bimolecular (A-2) process. In addition a unimolecular reaction involving methyl–oxygen cleavage would give the unlikely methyl carbonium ion. What is apparently occurring is an SN2 type of displacement on the methyl carbon of the protonated imidate, with a neutral amide as the leaving group. An analogous reaction has been

$$\text{H}_2\text{O}^{\frown}\text{CH}_3$$

$$\text{Ph-}\overset{\text{O}^+}{\underset{\|}{\text{C}}}\text{-N}\overset{\displaystyle <}{} \longrightarrow \text{H}_2\overset{+}{\text{O}}\text{-CH}_3 + \text{Ph-}\overset{\text{O}}{\underset{\|}{\text{C}}}\text{-N}\overset{\displaystyle <}{}$$

suggested as a possibility for the acid-catalyzed hydrolysis of carboxylate esters (the A_{A1}-2 reaction)[8] but has not yet been observed.

A further interesting facet of this reaction is its takeover in the more concentrated acids from the normal acid-catalyzed imidate hydrolysis (*i.e.*, tetrahedral intermediate and ester product). Changes in reaction mechanism with increasing acidity have been observed in the hydrolysis of carboxylate esters[9] and amides[10] but have all involved a change from a bimolecular to a unimolecular reaction. In this case the change involves the position of nucleophilic attack, the acyl carbon being the more reactive site in dilute acid and the methyl carbon in concentrated acid. The explanation for this behavior is not immediately apparent, but could lie in the hydration requirements for the two reactions. Work is currently in progress on this unusual behavior and will be reported at a later date.

Acknowledgment. This work was carried out with support from a grant from the National Research Council of Canada to Professor K. Yates, to whom I am grateful for fruitful discussions.

(7) C. R. Smith, Ph.D. Thesis, University of Toronto, 1971.
(8) J. N. E. Day and C. K. Ingold, *Trans. Faraday Soc.*, 37, 686 (1941).
(9) K. Yates, *Accounts Chem. Res.*, 4, 136 (1971).
(10) J. A. Duffy and J. A. Leisten, *J. Chem. Soc.*, 583 (1960); J. W. Barnett and C. J. O'Connor, *J. Chem. Soc., Perkin Trans. 2*, 2378 (1972).
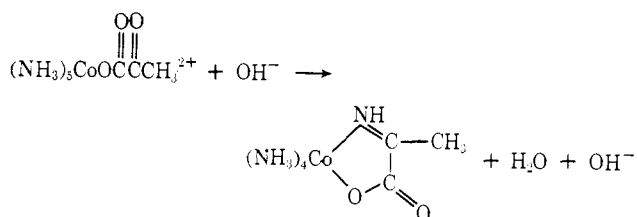
Robert A. McClelland

Department of Chemistry, University of Toronto
Toronto, Ontario, Canada M5S 1A1
Received January 23, 1974

Intramolecular Chelation *via* Imines. A Novel Condensation of Acetylacetone with Pyruvilidinatotetraamminecobalt(III) Ion

Sir:

The synthesis of the chelated imine species by a base-

$$(\text{NH}_3)_5\text{CoOC}\overset{\text{OO}}{\overset{\|\|}{\text{CCH}_3}}{}^{2+} + \text{OH}^- \longrightarrow$$

$$(\text{NH}_3)_4\text{Co}\overset{\text{NH}}{\underset{\text{O}\diagdown\text{C}\diagdown\text{O}}{\diagup\diagup}}\text{C-CH}_3 + \text{H}_2\text{O} + \text{OH}^-$$

catalyzed reaction of pyruvatopentaamminecobalt(III) ion has been described previously.[1] The imine species

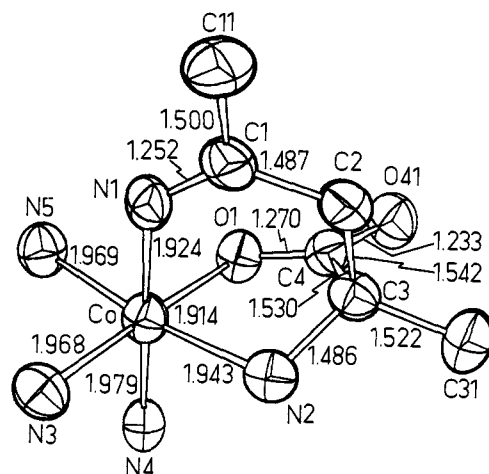(1) J. MacB. Harrowfield and A. M. Sargeson, *J. Amer. Chem. Soc.*, 96, 2634 (1974).

Figure 1. The overall stereochemistry of the cation. Typical bond length esd's are: Co–O, 0.004; Co–N, 0.005; C–O, 0.007; C–N, 0.007, C–C, 0.008 Å.

was readily deprotonated at the imine N center (pK ~ 10.5) and proton exchange was also observed at the methyl group. These properties indicated that it might condense with acetylacetone in a basic medium to give a chelated 3,5-dimethylpyridine-2-carboxylate ligand. Condensation of the carbonyl center at the imine site with elimination of H_2O followed by attack of the deprotonated methyl (–CH_2–) at the other carbonyl site, again with elimination of H_2O, would yield the pyridine species.

The pyruvilidinimine chloride (1.5 g in 25 ml of H_2O) was treated therefore with acetylacetone in basic aqueous solution (4 g of acacH in 25 ml of 1 M NaOH) at 25°. Condensation occurred over 24 hr and the product was isolated as the perchlorate (1.5 g) or dithionate. However, analysis indicated that only three new carbon atoms were incorporated into the product (*Anal.* Calcd for (CoC₆H₂₀N₅O₂(S₂O₆): Co, 14.26; C, 17.44; H, 4.88; N, 16.94; S, 15.52. Found: Co, 14.6; C, 17.49; H, 4.95; N, 16.83; S, 15.51). Pmr spectroscopy indicated the presence of one methyl group δ −2.30 (ppm relative to TMS) on the C atom of an –N=C< group and another methyl (δ −1.40) attached to a saturated carbon atom. A two-proton singlet at δ −2.98 was tentatively assigned to a methylene group flanked by the imino C atom and the saturated carbon atom. Signals at δ −2.65, −3.48, and −3.78 accounted for three coordinated ammonia molecules. Hence, one ammonia of the starting complex had disappeared being replaced by an imino NH (δ −10.26). The analysis and pmr results implied that acetylacetone had condensed with a coordinated ammonia through a >C=O center. Cleavage of acetylacetone and condensation at the imine center of the starting complex was also indicated.

A three-dimensional X-ray diffraction study of the dithionate salt has established that the complex cation has the structure shown in Figure 1. The crystals were monoclinic, space group $P2_1/c$, with $a = 7.576$ (4), $b = 18.209$ (7), $c = 14.068$ (6) Å, $\beta = 125.25$ (2)°, and $Z = 4$. Reflection data were collected on a Picker FACS-I four-circle diffractometer using graphite-crystal monochromated Cu Kα radiation [1479 unique reflections with $I/\sigma(I) \geq 3.0$]. Data have been corrected for absorption effects. Block-diagonal least-squares refine-

Scheme I
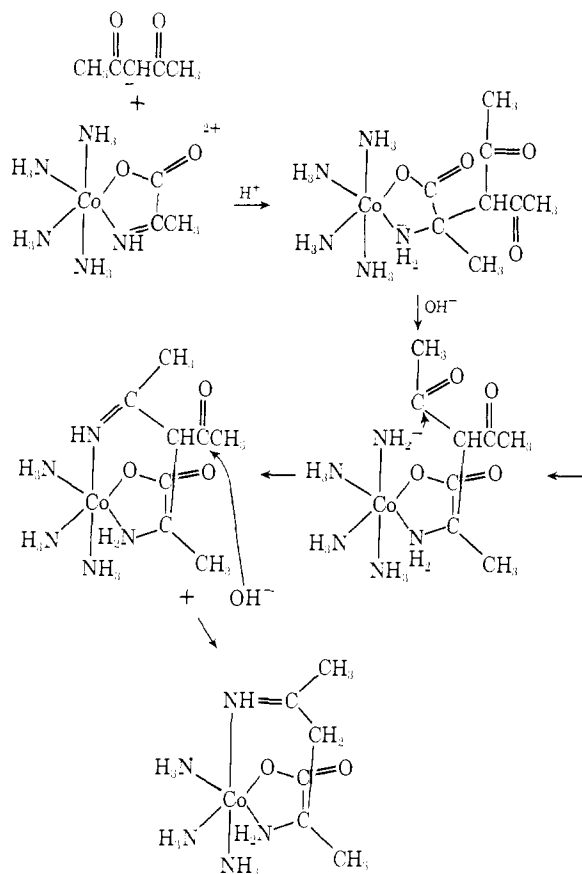
ment of all atomic positional parameters, anisotropic temperature factors for Co, S, O, N, and C atoms, isotropic thermal parameters for hydrogen atoms, and overall scale factor, has converged with $R = 0.040$.

The cation, which is essentially octahedral about the central cobalt atom shows the expected bond distances (see Figure 1). Two structural features are of special note. (1) The C–O distances in the coordinated carboxylate ion [i.e., C(4)–O(1), 1.270 (7); C(4)–O(41), 1.233 (6) Å] are significantly different. (2) The five-membered chelate ring is markedly aplanar, with C(3) and C(4) being 0.748 and 0.350 Å, respectively, from the plane of Co, N(2), O(1), in the direction of N(1). In contrast, the chelate ring in simple α-amino acid adducts is usually close to planar.[2] In the present complex, this aplanarity is probably a consequence of the tridentate character of the ligand.

The order of events for the addition of acetylacetone has not been elucidated, but, since the acetylacetone carbanion is readily formed and such species add rapidly to the coordinated imines,[1] it seems a reasonable initial step. Base-catalyzed condensation of a carbonyl center with the less acidic ($pK_a > 14$) apical ammonia should follow (Scheme I). It also seems reasonable to assert that the acetyl group is still intact at this stage and that hydrolysis occurs after the chelation process.

All three aspects are being examined. A benzoyl group may stabilize the acylated complex and if the pH is low enough the addition of carbanion may be observed separately from the condensation with coordinated NH_3.

(2) H. C. Freeman, Advan. Protein Chem., 22, 257 (1967).

The process generates a novel amino acid tridentate complex and an asymmetric center at the C atom where condensation occurs. Reactions of this type have value in their capacity to expand synthetic expertise in chelate chemistry and especially for the prospects they give in synthesizing multidentate complexes.

B. T. Golding, J. MacB. Harrowfield, G. B. Robertson
A. M. Sargeson,* P. O. Whimp
Research School of Chemistry, Australian National University
Canberra, A.C.T., Australia 2600

Optical Activity Associated with Isolated Olefinic Bonds. II. Experimental Evidence for the Role of π-Bond Torsion in Circular Dichroism Couplets and the Question of the $\sigma_a \rightarrow \pi_x{}^*$ Contribution[1]

Sir:

In earlier studies of olefin circular dichroism we proposed the allylic bond polarization (ABP) model to account for the sign of the low energy portion of the couplet observed for most endocyclic olefins.[1,2] In this we followed the suggestion of Scott and Wrixon[3] ascribing the couplet to $\pi_y{}^* \leftarrow \pi_x \rightarrow \pi_x{}^*$ with $\pi_x \rightarrow \pi_x{}^*$ representing the low energy portion. Levin and Hoffmann recently reported calculations of $\pi \rightarrow \pi^*$ rotatory strengths of model olefins,[4] suggesting that π-bond torsion sense is the dominant factor in the CD of twisted olefins. We now wish to present new data which constitutes: (1) support for the $\pi_y{}^* \leftarrow \pi_x \rightarrow \pi_x{}^*$ assignment for cyclohexene CD couplets, (2) the first *experimental evidence* establishing the characteristics of torsion induced olefin CD, and (3) the first observations suggesting an additional CD active transition in the region of the uv dominant $\pi \rightarrow \pi^*$ transitions. We consider this new band to be the $\sigma_a \rightarrow \pi_x{}^*$ transition previously placed in this energy span by various calculations.[5]

The assignment of the CD couplet to the two $\pi \rightarrow \pi^*$

(1) For part I see N. H. Andersen, C. R. Costin, D. D. Syrdal, and D. P. Svedberg, J. Amer. Chem. Soc., 95, 2049 (1973).

(2) The ABP model[1] and the Scott–Wrixon dissignate octant rule[3] are closely related. In the ABP model attention is focused on the chiral relationship of the more polarizable allyl bonds and the π orbital rather than the carbon framework as a whole. See W. Klyne and D. N. Kirk, Tetrahedron Lett., 1483 (1973), for a definition of the useful term, dissignate.

(3) (a) A. I. Scott and A. D. Wrixon, Chem. Commun., 1182 (1969); (b) Tetrahedron, 26, 3695 (1970); (c) ibid., 27, 4787 (1971).

(4) C. C. Levin and R. Hoffmann, J. Amer. Chem. Soc., 94, 3446 (1972).

(5) A. J. Merer and R. S. Mulliken, Chem. Rev., 69, 639 (1969). See also ref 3b. The lower energy Rydberg transition, $\pi_x \rightarrow 3s$, apparently occurs in this region in some solvents; however, its contribution to the CD of olefins of this report is minimal as judged by the absence of solvent effects.[6]

(6) There is some dispute as to the assignment of the low energy CD band of highly substituted olefins. Burgstahler, Barkhurst, and Gawronski have suggested that it is associated with a transition between a π state and a σ_a state ($\sigma_a \rightarrow \pi_x{}^*$ or $\pi_x \rightarrow 3s$).[7] The $\pi_x \rightarrow 3s$ transition has been implicated in the solvent dependent CD of $(-)$-α-pinene;[8] however, we have determined the CD spectra of a number of the endocyclic olefins of the table in a series of solvents (n-pentane, CH_3CN, perfluoroheptane, and hexafluoro-2-propanol) and find no significant polarity or density dependence for λ_2, $\Delta\Delta\epsilon$, or Δ_{ij}.[9] On this basis we conclude that the $\pi_x \rightarrow 3s$ transition is not a major contributor to either band of the CD couplets observed.

(7) A. W. Burgstahler, R. C. Barkhurst, and J. R. Gawronski in "Modern Methods of Steroid Analysis," E. Heftmann, Ed., Academic Press, New York, N. Y., 1973. The authors acknowledge the receipt of this manuscript prior to publication.

(8) A. E. Drake and S. F. Mason, J. Chem. Soc., Chem. Commun., 253 (1973).

(9) N. H. Andersen and Y. Ohta, submitted for publication.