

invaluable advice. We are also indebted to Mrs. A. L. Klopfer for much of the experimental work.

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### The Structure of Acetatopentaamminecobalt(III) in $[\text{Co}(\text{NH}_3)_5(\text{CH}_3\text{CO}_2)](\text{Cl})(\text{ClO}_4)^1$

Sir:

The recent suggestion by Fraser<sup>2</sup> that the bonding of the carboxylato groups in carboxylatopentaamminecobalt(III) complexes is an ionic bidentate linkage with both oxygen atoms equivalent led us to investigate the structure of the acetatopentaamminecobalt(III) complex.

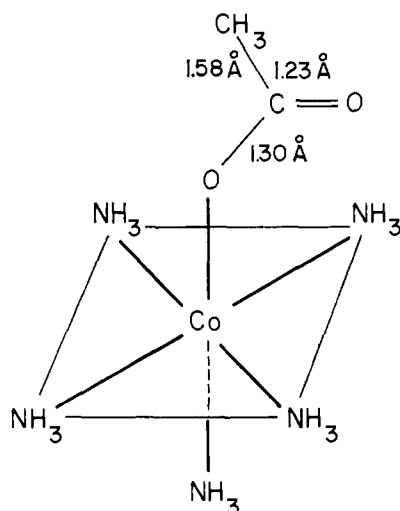


Figure 1. Structure of the acetatopentaamminecobalt(III) ion. The average Co(III)-N distance is 2.00 Å; standard deviations in bond distances  $\sim 0.02$ - $0.03$  Å.

Although the acetate group is known to act as a bidentate ligand in some of its complexes,<sup>3</sup> the structure proposed by Fraser contradicts some chemical evidence<sup>4</sup>; also, a seven-coordinate cobalt(III) species seemed unlikely. The crystal studied was  $[\text{Co}(\text{NH}_3)_5(\text{CH}_3\text{CO}_2)](\text{Cl})(\text{ClO}_4)$ .<sup>5</sup> The crystal is orthorhombic with cell constants  $a = 22.01$ ,  $b = 9.75$ ,  $c = 11.41$  Å.; the space group is *Pbca*. The measured density is 1.84 g./cm.<sup>3</sup> (the calculated density is 1.83 g./cm.<sup>3</sup>) which requires eight molecules per unit cell. The intensity data were collected with Mo radiation with a set of balanced filters using a GE XRD5 with a scintillation counter. The residual for the 1143 observed

(1) This research was generously supported by grants from the Public Health Service and A.R.P.A.

(2) R. T. M. Fraser, *Nature*, **202**, 691 (1964).

(3) J. van Nieckeck, F. Schoening, and J. Talbot, *Acta Cryst.*, **6**, 720 (1953); W. H. Zachariasen and H. A. Plettinger, *ibid.*, **12**, 526 (1960).

(4) H. Taube, private communication; this refers to the fact that in the acetatopentaamminecobalt(III) the two oxygen atoms of the acetate group exchange with solvent oxygens at different rates, suggesting a nonequivalence of the oxygen atoms (see R. B. Jordan, Thesis, University of Chicago, 1965).

(5) The crystals were obtained by recrystallizing a sample of the perchlorate salt of the complex, kindly supplied by J. Halpern, in KCl solution with the intention of preparing the dichloride salt; instead, the chloride-perchlorate salt was obtained.

reflections was 14%. The hydrogen atoms were not included in the calculations.

The structure for the acetatopentaamminecobalt(III) is shown in Figure 1. It is clear that the acetate is bonded to the cobalt by a monodentate linkage and that the two oxygen atoms of the acetate are non-equivalent. The bond distances in the structure are similar to those found in related structures.<sup>6</sup>

The carbonyl oxygen atom of the acetate is about equidistant from two ammonia nitrogen atoms with distances that indicate it is participating in hydrogen bonding with these nitrogen atoms.

The carbonate group was recently found to act as a monodentate ligand in the complex,  $[\text{Co}(\text{NH}_3)_5\text{CO}_3] \cdot \text{Br} \cdot \text{H}_2\text{O}$ .<sup>7</sup>

*Acknowledgment.* We wish to thank J. Halpern for bringing this problem to our attention.

(6) G. Palenik, *Acta Cryst.*, **17**, 360 (1964); Y. Shigeta, Y. Komryama, and H. Kuroya, *Bull. Chem. Soc. Japan*, **63**, 1159 (1963).

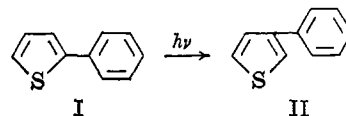
(7) H. C. Freeman and G. Robinson, *J. Chem. Soc.*, 3184 (1965).

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### The Photochemical Rearrangement of Arylthiophenes

Sir:

When 2-phenylthiophene (I) is illuminated with ultraviolet light for 38 hr. at 80° in benzene solution, 3-phenylthiophene (II) is formed in good yield.



Thus when 98 mg. of 2-phenylthiophene, m.p. 34.5-35°,<sup>1</sup> in 87 g. of benzene to which 6.5 g. of crystallized sodium thiosulfate was added was irradiated with a Hanau S-81<sup>2</sup> mercury high-pressure lamp and the reaction monitored using quantitative vapor phase chromatography,<sup>3</sup> nearly all of the 2-phenylthiophene had disappeared after 38-hr. irradiation, while about 40 mg. of 3-phenylthiophene was formed. Preparative v.p.c. then enabled the isolation of the major component 3-phenylthiophene, m.p. 90-91°, mixture melting point undepressed; infrared and ultraviolet spectra are identical with those of authentic 3-phenylthiophene.<sup>4</sup>

(1) The substance was made by the method of J. L. Melles and H. J. Backer, *Rec. trav. chim.*, **72**, 314 (1953); melting points: A. S. Brown and M. G. Voronkov, *Dokl. Akad. Nauk SSSR*, **59**, 1293 (1948); *Chem. Abstr.*, **43**, 2614 (1949); infrared spectra: A. R. Katritzky and A. J. Boulton, *J. Chem. Soc.*, 3500 (1959); J. S. Sørensen and N. A. Sørensen, *Acta Chem. Scand.*, **12**, 773 (1958); ultraviolet spectrum: L. Bruzzi, J. Degani, and A. Tundo, *Boll. Sci. Fac. Chim. Ind. Bologna*, **19**, 40 (1961).

(2) A. Schönberg, "Präparative Organische Photochemie," Springer Verlag, Vienna, 1958, p. 126.

(3) F. & M. Model 810 apparatus with flame ionization detection; immobile phase diethylene glycol succinate (LAC-728); column temperature 190°, using He as carrier gas (60 ml./min.).

(4) Synthesis and melting point: J. L. Melles and H. J. Backer, *Rec. trav. chim.*, **72**, 491 (1953); infrared spectrum: H. Rosatzin, *Spectrochim. Acta*, **19**, 1107 (1963); J. Degani, M. Pallotti, and A. Tundo, *Ann. Chim. (Rome)*, **51**, 434 (1961); ultraviolet spectrum: see Bruzzi, *et al.*<sup>1</sup>