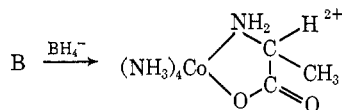
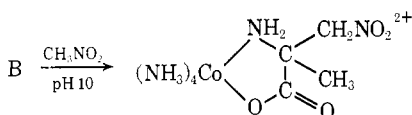


mated value of 16 for the  $pK_a$  of coordinated  $NH_3$  at  $Co(III)$ .<sup>5</sup>

Several reactions characteristic of imines<sup>6</sup> support the proposal for the pyruvilidene-imine structure. Reduction with  $BH_4^-$  ion rapidly generates alaninatotetraamminecobalt(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,



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  $\delta -1.49$  ppm ( $CHCH_3$ ) and a quartet centered at  $\delta -3.73$  ppm ( $CHCH_3$ ). Michael addition of carbanions occurred rapidly. For example nitromethane in aqueous  $Na_2CO_3$  buffer (pH 10) gave



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<sup>1</sup> 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<sup>2</sup> to exert a comparable effect in a ruthenium(II) complex. The sulfur bound sulfitopentaamminecobalt(III) cation has been shown to possess an extremely large kinetic trans effect.<sup>3</sup> Since an X-ray structure determination<sup>4</sup> for *trans*-Co(en)<sub>2</sub>-SO<sub>3</sub>NCS shows no significant lengthening of the cobalt-thiocyanate bond, the kinetic effect has been ascribed<sup>5</sup>

(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).

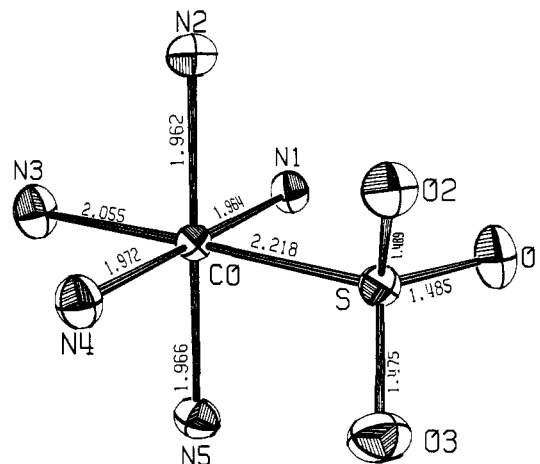


Figure 1. A perspective view of  $[(NH_3)_5CoSO_3]^+$ . The ellipsoids represent 50% probability.

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.<sup>6</sup> 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,<sup>7</sup>  $Z = 4$ ;  $d_{calcd} = 1.87$ ,  $d_{measd} = 1.87$  (2) g cm<sup>-3</sup>. 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<sup>8</sup> of 0.028 and a weighted  $R$  factor<sup>9</sup> of 0.032. The 1979 unique reflections used for refinement were measured with a Syntex PI 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  $[(NH_3)_5CoSO_3]^+$  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. Gröger, *Z. Anorg. Chem.*, **16**, 398 (1898).

(7) "International Tables for X-Ray Crystallography," Vol. 1, 2nd ed, Kynoch Press, Birmingham, England, 1965.

(8)  $R = \sum |F_o| - |F_c| / \sum |F_o|$ .

(9)  $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w(F_o)^2]^{1/2}$ .

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