

about 13 kcal/mole (the resonance energy of the allylic radical<sup>8e</sup>), thus leading to a predicted and observed activation energy for formation of an intermediate in the vinylcyclopropane isomerization of 50 kcal/mole. The diradical can cause geometrical isomerization of the deuterium label just as it does in cyclopropane. In addition this diradical can by redistribution of electrons and slight movement of some carbon and hydrogen nuclei rearrange to cyclopentene. We propose this scheme as a logically structured, and presently acceptable, mechanism. However, we would also point out that an alternative scheme that would consider cyclopentene formation and geometrical isomerization to be in separate energy manifolds is only so slightly different both conceptually and experimentally from the diradical mechanism that we cannot discount it without further, and more subtle, experiments.<sup>8</sup>

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(8) A suggestion that this alternative explanation may be quite reasonable is provided by Hoffmann's calculations of the stereochemical course of the closure of trimethylene diradicals,<sup>9</sup> Crawford's observations on the behavior of these diradicals generated from pyrazoline pyrolysis,<sup>10</sup> and Rabinovitch, Setser, and Wiberg's expanded ring model for cyclopropane isomerization.<sup>6a,7</sup>

(9) R. Hoffmann, Abstracts of the 151st National Meeting of the American Chemical Society, Pittsburgh, Pa., March 1966, Paper 109K.

(10) R. J. Crawford and A. Misra, *J. Am. Chem. Soc.*, **88**, 3963 (1966).

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### Five-Coordinate Copper(II) in [Cu(tren)(NCS)](SCN)

Sir:

Raymond and Basolo<sup>1</sup> have recently reported the preparation of [Cu(tren)(NCS)](SCN)<sup>2</sup> and have suggested that one thiocyanate ion is coordinated to the copper(II) ion through the nitrogen atom and the other through the sulfur atom, in a *cis*-octahedral complex. Their conclusion was based upon two observations. First, the appearance of two C-N frequencies at 2094 and 2060 cm<sup>-1</sup> and two C-S frequencies at 818 and 745 cm<sup>-1</sup> in the infrared spectrum suggested that one thiocyanate is bonded to copper through the nitrogen atom and the other is either bonded through the sulfur atom or not coordinated to copper. Secondly, the similarity in cell dimensions and identity of space group of the crystalline copper and nickel compounds suggested that the two molecules have the same configuration, and Rasmussen<sup>3</sup> has shown Ni(tren)(NCS)<sub>2</sub> to have a *cis*-octahedral configuration.

Professor Basolo kindly furnished us a sample of [Cu(tren)(NCS)](SCN), and we have determined its crystal structure. The cell has dimensions  $a = 9.16$ ,  $b = 14.00$ ,  $c = 11.29$  Å and contains four molecules. Systematic absence of  $h00$ ,  $0k0$ , and  $00l$  with odd indices indicates the space group P2<sub>1</sub>2<sub>1</sub>2<sub>1</sub>. (The cell dimensions for the nickel compound are  $a = 8.62$ ,  $b = 14.72$ ,  $c = 10.82$  Å, and its space group is also P2<sub>1</sub>2<sub>1</sub>2<sub>1</sub>.)

(1) K. N. Raymond and F. Basolo, *Inorg. Chem.*, **5**, 1632 (1966).

(2) tren = N(CH<sub>2</sub>CH<sub>2</sub>NH<sub>2</sub>)<sub>3</sub>.

(3) S. E. Rasmussen, *Acta Chem. Scand.*, **13**, 2009 (1959).

Table I. Bond Lengths (in Angstroms) and Angles (in Degrees)

Cu-N(1)	2.04	N(1)-Cu-N(2)	84
Cu-N(2)	2.07	N(1)-Cu-N(3)	85
Cu-N(3)	2.16	N(1)-Cu-N(4)	85
Cu-N(4)	2.06	N(5)-Cu-N(2)	95
Cu-N(5)	1.95	N(5)-Cu-N(3)	98
		N(5)-Cu-N(4)	94
		N(1)-Cu-N(5)	177
		N(2)-Cu-N(3)	114
		N(2)-Cu-N(4)	130
		N(3)-Cu-N(4)	113

Three-dimensional X-ray diffraction intensities were collected on a Picker single-crystal diffractometer with Mo K $\alpha$  radiation, out to a limit of  $2\theta = 55^\circ$ . The positions of the copper atoms were determined from a sharpened Patterson synthesis, and the other atoms were found in a series of Fourier syntheses. The structure has been refined by full-matrix least squares, with isotropic temperature factors and without introduction of hydrogen atoms, to a value of  $R = 0.08$ . The refinement is being continued and the final results will be published later.

The copper ion is surrounded by five nitrogen atoms from the tren molecule and one thiocyanate ion, in a somewhat distorted trigonal bipyramid, with the tertiary nitrogen atom, N(1), and the thiocyanate nitrogen atom, N(5), at the apices, and the three primary nitrogen atoms, N(2), N(3), N(4), in the equatorial positions. Bond lengths and angles in the coordination polyhedron are given in Table I. The nitrogen atom, N(6), of the second thiocyanate ion lies at a distance of 3.84 Å from the copper ion in the equatorial plane of the trigonal bipyramid, near the bisector of the N(2)-Cu-N(3) angle. The Cu-N(6)-S(2) angle is  $96^\circ$ , bringing the S(2) atom to 3.7 Å from N(3) but more than 5 Å from Cu. The S(2) atom from another thiocyanate ion is 4.57 Å from the copper ion, and this is the shortest Cu-S distance in the crystal. Thus the second thiocyanate ion is not coordinated to the copper ion.

The apparently reasonable, but incorrect, conclusions of Raymond and Basolo regarding the structure of [Cu(tren)(NCS)](SCN) illustrate the danger of drawing structural conclusions from comparisons of cell dimensions and the space group of crystals.

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### Arylation by Aromatic Nitro Compounds at High Temperatures

Sir:

Since Berthelot in 1887 established the explosiveness of nitroaromatics at high temperatures,<sup>1</sup> there has been an understandable reluctance on the part of chemists to study the reactions of these derivatives at 400° and higher. What scant literature exists is concerned with determination of safe temperature limits, e.g., for hydrogenation of nitroxylenes to xylidines.<sup>2</sup>

(1) M. Berthelot, *Compt. Rend.*, **105**, 1159 (1887).

(2) R. L. Datta and N. R. Chatterjee, *J. Chem. Soc.*, **115**, 1006 (1919); C. L. Brown, W. M. Smith, and W. G. Scharmann, *Ind. Eng. Chem.*, **40**, 1538 (1948); P. C. Condit and R. L. Haynor, *ibid.*, **41**, 1700 (1949).