

- 1975, Chapter 2.
- (14) The differentiable permutations are  $h_2 = (1)(23)^v$ ,  $h_3 = (12)(3)^v$ ,  $h_4 = (13)(2)^v$ ,  $h_5 = (123)^v$ ,  $h_6 = (132)^v$ ,  $h_7 = (1)(2)(3)^v$ ,  $h_8 = (1)(23)^v$ ,  $h_9 = (12)(3)^v$ ,  $h_{10} = (13)(2)^v$ ,  $h_{11} = (123)^v$ ,  $h_{12} = (132)^v$ , where configuration  $v$  is determined by  $(B, C, D) = (1, 2, 3)$  and  $v^*$  is the enantiomer of  $v$ .
- (15) Simulated spectra were calculated with the Whitesides classical multisite exchange computer program EXCHSYS.<sup>16</sup>
- (16) G. M. Whitesides and J. S. Fleming, *J. Am. Chem. Soc.*, **89**, 2855 (1967).
- (17) If resonance C is assigned to H(14), no mechanistic conclusions follow.
- (18) Rate constants determined by visual matching of calculated and experimental spectra were analyzed (weighted least squares, 10 points for  $h_{10}$ , 7 points for  $h_9$ ) by the linearized Eyring equation. Standard deviations in the derived parameters are given in parentheses.
- (19) If the assumption that all four hydrogen ligands must move is relaxed, the configurations connected by  $h_{10}$  can be interconverted by movements of  $H_B$ ,  $H_C$ , and  $H_D$  to adjacent faces,  $H_A$  remaining fixed; for  $h_9$  only  $H_D$  would move. It is not obvious why these particular partially face-bridged intermediates would be unique; we prefer the more symmetrical all-terminal intermediates.
- (20) Extended Hückel calculations (R. Hoffmann, et al., *J. Am. Chem. Soc.*, submitted for publication) on  $H_4Fe_4(CO)_{12}$  (carbonyls staggered) indicate relatively little energy difference between face-bridging and edge-bridging (as in either  $H_4Ru_4(CO)_{12}$  or **1**) positions for the hydrogen ligands. Terminal positions were not examined.
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### Single-Crystal Properties of $[Co(C_5H_5NO)_6](NO_3)_2$

Sir:

Several transition metal complexes of pyridine *N*-oxide have been investigated carefully at low temperatures recently, and some remarkably interesting results have been obtained. The series of compounds  $M(C_5H_5NO)_6X_2$ , with  $X$  being either perchlorate or fluoborate, and  $M^{II}$  an iron series ion, are rhombohedral and isostructural.<sup>1,2</sup> In the case of the cobalt compounds, magnetic ordering is observed at 0.357 K ( $BF_4^-$ ) and 0.428 K ( $ClO_4^-$ ), and the molecules provide the only examples to date of the simple cubic,  $S = 1/2$ , XY model antiferromagnet.<sup>3-6</sup> The compound  $[Ni(C_5H_5NO)_6](ClO_4)_2$  exhibits<sup>7</sup> a very large zero-field splitting of 6.3 K, and the crystal structure and other features of this molecule are such that it provides the first example of a magnetic-field-induced antiferromagnetic phase transition.<sup>8,9</sup> Large zero-field splittings allow the ferrous analogue to be an excellent example of the three-dimensional Ising model,<sup>10</sup> while the copper compounds distort as they are cooled in such a fashion that the perchlorate becomes a one-dimensional antiferromagnet, and the fluoborate provides the best example of the two-dimensional Heisenberg,  $S = 1/2$  antiferromagnet.<sup>11</sup>

The great success obtained with the above studies has suggested that it may be profitable to extend these studies by examining the analogous series of nitrates,  $[M(C_5H_5NO)_6](NO_3)_2$ , and we report here results that in fact appear to confirm this hypothesis. All the salts of the iron series ions have been prepared and found to be isostructural, but we restrict this report to the cobalt analogue.

Deep-red  $[Co(C_5H_5NO)_6](NO_3)_2$  is prepared in the same manner as were the perchlorates<sup>12</sup> and single crystals with satisfactory elemental analysis may be grown from DMF. Using precession camera techniques, we find that the compound belongs to the space group  $R\bar{3}$ , with  $a = 9.487 \text{ \AA}$  and  $\alpha = 83^\circ 21'$ . The measured density is  $1.50 \text{ g/cm}^3$ , and calculated,

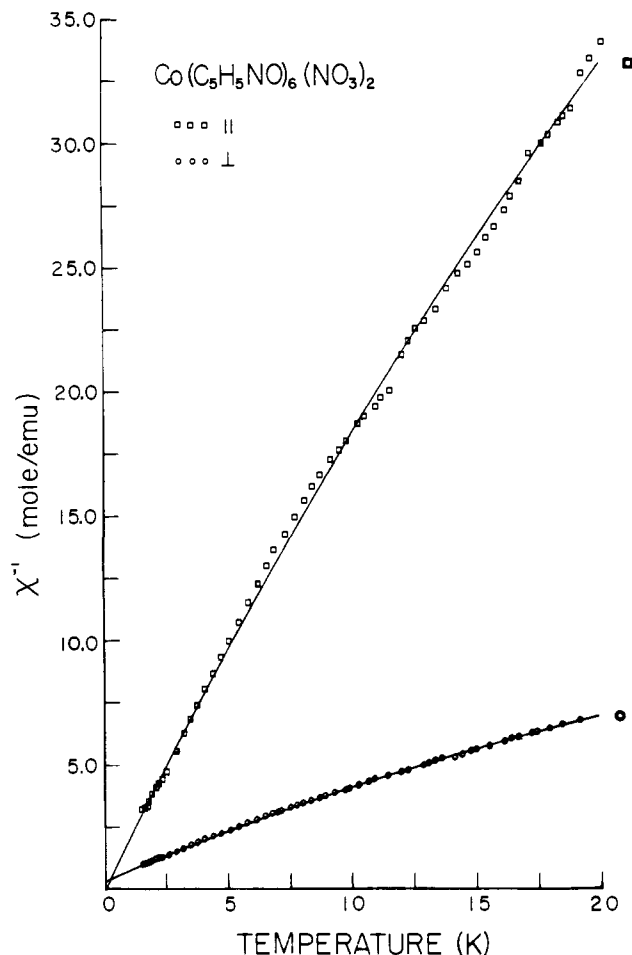


Figure 1. Curie-Weiss plots of the magnetic susceptibilities of  $[Co(C_5H_5NO)_6](NO_3)_2$ :  $\square$ ,  $\parallel$ ;  $\circ$ ,  $\perp$ .

for one molecule in this rhombohedral unit cell, is  $1.493 \text{ g/cm}^3$ . Since the analogous perchlorate compound also belongs<sup>2</sup> to the same space group, with  $a = 9.617 \text{ \AA}$ ,  $\alpha = 81.16^\circ$ ,  $Z = 1$ , and the fluoborate analogue is isostructural,<sup>1</sup> one may conclude that the three crystals are isostructural. This observation led us to measure the single-crystal magnetic susceptibilities of the nitrate, in anticipation that they would be similar to those of the perchlorate, and give us guidance on the magnetic ordering behavior to be expected.

The guide to the discovery of XY magnets lies with the  $g$ -value anisotropy of the metal atom.<sup>4</sup> In particular, the  $g$  tensor should have uniaxial symmetry, with  $g_{\perp} \gg g_{\parallel}$ . These conditions were substantially fulfilled by the perchlorate compound, for which susceptibility measurements yielded  $g_{\parallel} = 2.49$  and  $g_{\perp} = 4.70$ . The inverse isothermal susceptibilities of  $[Co(C_5H_5NO)_6](NO_3)_2$  are plotted as a function of temperature in Figure 1. Normal Curie-Weiss behavior is observed, with the following set of parameters:  $g_{\parallel} = 2.27 \pm 0.05$ ,  $g_{\perp} = 4.83 \pm 0.05$ ,  $\theta_{\parallel} = 0.0 \pm 0.05 \text{ K}$ ,  $\theta_{\perp} = -0.61 \pm 0.05 \text{ K}$ ,  $TIP(\parallel) = 0.006 \text{ emu/mol}$ , and  $TIP(\perp) = 0.037 \text{ emu/mol}$ . The sign of  $\theta_{\perp}$  is antiferromagnetic. These results suggest that  $[Co(C_5H_5NO)_6](NO_3)_2$  ought to be as good an example of the XY model magnet as the earlier cases, and probably a better one, since the  $g$ -value anisotropy is even greater for the nitrate. Furthermore, the crystallographic angle  $\alpha$  is slightly larger, tending toward the simple cubic value of  $90^\circ$ . This is important in determining the superexchange path, as well as ensuring that a reference cobalt ion is connected to its six nearest magnetic neighbors by equivalent superexchange paths.

With  $\theta_{\perp} = -0.61 \text{ K}$ , an exchange constant of  $J/k = -0.2$

K can be derived if six nearest magnetic neighbors are assumed. The antiferromagnetic ordering temperature will be below 1 K. These results are corroborated by specific heat studies on this compound,<sup>13</sup> which are found to yield a sharp  $\lambda$ -type anomaly at  $T_c = 0.456$  K, an ordering temperature slightly higher than that of the perchlorate.

The superexchange path in  $[\text{Co}(\text{C}_5\text{H}_5\text{NO})_6](\text{ClO}_4)_2$  and  $[\text{Co}(\text{C}_5\text{H}_5\text{NO})_6](\text{BF}_4)_2$  has been assigned<sup>4</sup> a Co-O-O-Co interaction, with an O-O separation of 5.6 Å. It is especially important that the rings turn away, in propeller fashion, from the metal atoms. The great similarity in the properties displayed by the nitrate suggests that the same superexchange path is available here. Final discussion awaits a full crystal structure analysis, which is in progress. One is also led to suggest that O-O contact on neighboring molecules not only provides a suitable exchange path, but may also be a contributing factor to the particular crystal lattice structure assumed by these molecules.

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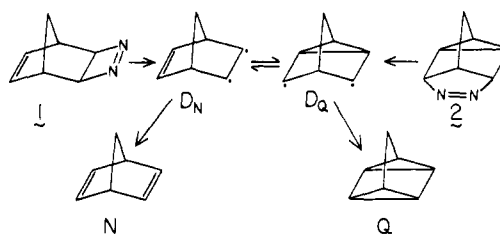
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## Energy Acquisition, Storage, and Release. Photochemistry of Cyclic Azoalkanes as Alternate Entries to the Energy Surfaces Interconnecting Norbornadiene and Quadricyclene

Sir:

The photochemical rearrangement of norbornadienes to quadricyclenes is a useful reaction of wide synthetic scope.<sup>1</sup> We selected the cyclic azoalkanes **1** and **2** as potential precursors to the norbornadienyl and quadricyclenyl diradicals ( $D_N$  and  $D_Q$ ), respectively. It was anticipated that a quantitative investigation of the photochemistry of **1** and **2** would reveal significant information relevant to the mechanism of the photointerconversions of the parent systems norbornadiene (N), and quadricyclene (Q) by providing independent routes to  $D_N$  and  $D_Q$  and thereby assist in elucidating the nature of the energy surfaces along which N and Q may be interconverted<sup>4</sup> (Scheme I).

Scheme I. Reactions of **1** and **2** to form N and Q.



The photolysis of **1** and **2** under a variety of conditions led<sup>2,3</sup> to loss of  $\text{N}_2$  and formation of N and Q in nearly quantitative yield and with good quantum efficiencies (Table I). In all cases care was taken to assure that N and Q were formed as primary products and not via secondary thermal or photochemical processes.

The yields of Q and N are ~90% and 10%, respectively, upon triplet sensitization of **1** or **2** as well as upon *direct*  $S_0 \rightarrow T_1$  excitation<sup>5</sup> of **1** or **2**. From these results we conclude that the triplet state of **1** or **2** upon loss of  $\text{N}_2$  yields a triplet diradical which proceeds with high selectivity to Q.<sup>6</sup> Upon direct  $S_0 \rightarrow S_1$  excitation of **1**, the relative yields of N and Q are similar to those achieved by triplet sensitization; thus, we conclude that **1** undergoes efficient intersystem crossing from its  $S_1$  state. In contrast, the direct  $S_0 \rightarrow S_1$  excitation of **2** yields N as the *major* product, from which we conclude the intersystem crossing is *inefficient* from  $S_1$  of **2**.<sup>7</sup>

From the data in Table I, it appears that, if diradicals  $D_N$  or  $D_Q$  are produced in a singlet state, they proceed preferentially to yield N. In contrast, if  $D_N$  or  $D_Q$  are produced in a triplet state, preferential formation of Q is observed.

An exceedingly intriguing and important problem in understanding photochemical reactions concerns the geometry for which radiationless transitions occur from upper surfaces to the  $S_0$  surface.<sup>9</sup> Diradicaloid geometries have been postulated to serve as guides to the regions on excited surfaces through which molecules may "jump" to the ground-state surface.<sup>9</sup> It is thus anticipated that the favored geometry for a radiationless transition to  $S_0$  may be determined by the geometry of the minimum on the  $S_1$  or  $T_1$  surface which best serves to deliver excited molecules back to  $S_0$ .

Our results suggest that *the excited singlet surface connecting the N and Q structures possesses a minimum which*

Table I. Photochemistry of Azoalkanes **1** and **2**

Compd	Reaction conditions	$\phi$	% N	% Q
<b>1</b>	$S_0 \rightarrow S_1$ (RT) <sup>a</sup>	0.36 <sup>b</sup>	29 <sup>c</sup>	71 <sup>c</sup>
	$S_0 \rightarrow S_1$ (-78 °C)		9	91
	$S_0 \rightarrow T_1$ (RT) <sup>d</sup>		10	90
	<sup>3</sup> Sens (RT)	0.40 <sup>e</sup>	10	90
	<sup>3</sup> Sens (-78 °C) <sup>f</sup>		12	88
	Thermolysis <sup>g</sup>		~95	~5
<b>2</b>	$S_0 \rightarrow S_1$ (RT) <sup>a</sup>	0.44 <sup>b</sup>	63 <sup>c</sup>	37 <sup>c</sup>
	$S_0 \rightarrow S_1$ (-78 °C)		29	71
	$S_0 \rightarrow T_1$ (RT) <sup>d</sup>		11	89
	<sup>3</sup> Sens (RT)	0.57 <sup>e</sup>	10	90
	<sup>3</sup> Sens (-78 °C) <sup>f</sup>		10	90
	Thermolysis <sup>g</sup>		~100	0

<sup>a</sup> Pentane solvent unless noted otherwise. <sup>b</sup> Based on azoalkane disappearance and product formation. <sup>c</sup> Percentages include only N, Q products. At times small amounts of norbornene, toluene, and cycloheptatriene were observed but not included in percentages. <sup>d</sup> See ref 5. <sup>e</sup> Based on product formation. <sup>f</sup> The solvent was  $\text{CFCl}_3$ . At room temperature, the results in  $\text{CFCl}_3$  were the same as in pentane. <sup>g</sup> Thermolysis temperature 90–110 °C. Quadricyclene was shown to be stable under the reaction conditions.