

Figure 5. Magnetic field dependence of magnetization for CrMnSb at 77 K.

Table II. Magnetic Parameters

compd	$T_c$ or $T_N$ /K	$\theta_p$ /K	$n_p/\mu_B$	$n_F/\mu_B$
TiMnSb		-30	2.13	
VMnSb	25 <sup>a</sup>	34	4.37	
CrMnSb	198 <sup>b</sup>	223	3.50	1.17

<sup>a</sup>  $T_N$ . <sup>b</sup>  $T_c$ .

Curie temperature of 34 K. Since the sample obeyed the Curie-Weiss law in the paramagnetic region, the effective Bohr magneton per formula was calculated to be  $4.37 \mu_B$ . On the other hand, the compound CrMnSb was ferromagnetic with a Curie temperature of 198 K as shown in Figure 4. Since the paramagnetic Curie temperature had a positive value of 223 K, it is expected that the dominant magnetic interaction in CrMnSb was ferromagnetic. The field dependence of the magnetization at 77 K is shown in Figure 5. It is seen that the magnetization saturated at  $320 \text{ kA m}^{-1}$  ( $4.0 \text{ kOe}$ ) and the ferromagnetic moment per formula was calculated to be  $1.17$ . No magnetic ordering of TiMnSb was found down to 10 K, and the effective Bohr magneton per formula was calculated to be  $2.13 \mu_B$  from the slope of a  $\chi_M^{-1}-T$  curve. The magnetic parameters of these three compounds are tabulated in Table II. Although the MMnSb compounds contained twice as many transition-metal atoms per formula unit as the MSb compounds with the NiAs type structure, values of  $n_p$  of the former were not larger than those of the latter.<sup>1</sup> The magnetic properties of the present three compounds were different from each other. It is believed that these facts can be explained by a schematic 3d band model on the basis of that of MSb compounds with the NiAs type structure proposed by Goodenough,<sup>1</sup> but the detailed results have not yet been examined.

Registry No. TiMnSb, 88430-85-7; VMnSb, 88430-86-8; CrMnSb, 87716-72-1.

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### Photochemistry in Liquid Krypton: Generation and Thermal Stability of $\text{Fe}(\text{CO})(\text{N}_2)(\text{NO})_2$ and $\text{Fe}(\text{N}_2)_2(\text{NO})_2$

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We have recently demonstrated the value of noble gases as low-temperature solvents for both synthetic<sup>1</sup> (e.g.,  $\text{Cr}(\text{CO})_{6-x}(\text{N}_2)_x$ ) and mechanistic studies<sup>2</sup> ( $\text{Ni}(\text{CO})_3\text{N}_2$  CO

Table I. Observed Wavenumbers ( $\text{cm}^{-1}$ ) of  $\text{Fe}(\text{CO})_{2-x}(\text{N}_2)_x(\text{NO})_2$  Species in Liquid Krypton Solution and Solid  $\text{N}_2$  Matrices and Force Constants ( $\text{N m}^{-1}$ )

liquid Kr (155 K)	calcd <sup>a</sup>	$\text{N}_2$ matrix <sup>b</sup> (10 K)	assgnt <sup>c</sup>
$\text{Fe}(\text{CO})_2(\text{NO})_2$			
2086.9	2087.1	[2090]	$a_1 \nu_{\text{C-O}}$
2038.5	2038.0	[2081]	$b_1 \nu_{\text{C-O}}$
		[2038]	
1817	1816.8	[1820]	$a_1 \nu_{\text{N-O}}$
		[1817]	
1775.8	1774.8	[1779]	$b_2 \nu_{\text{N-O}}$
		[1775]	
2073.1 <sup>d</sup>	2073.0		$a' \nu^{13}\text{C-O}$
2006.5 <sup>d</sup>	2006.1		$a'' \nu^{13}\text{C-O}$
1805.3 <sup>d</sup>	1806.1		$a' \nu^{15}\text{N-O}$
1751.7 <sup>d</sup>	1753.4		$a'' \nu^{15}\text{N-O}$
$\text{Fe}(\text{CO})(\text{N}_2)(\text{NO})_2$			
2257.5		[2270]	$a' \nu_{\text{N-N}}$
		[2268]	
		[2262]	
2046.0		[2054]	$a' \nu^{12}\text{C-O}$
		[2050]	
		[2048]	
2001.0 <sup>d,e</sup>			$a' \nu^{13}\text{C-O}$
1805.1		[1806]	$a' \nu_{\text{N-O}}$
		[1804]	
1761.5		[1762]	$a'' \nu_{\text{N-O}}$
		[1760]	
$\text{Fe}(\text{N}_2)_2(\text{NO})_2$			
2250.5		2256 <sup>f</sup>	$a_1 \nu_{\text{N-N}}$
2228.0		2241 <sup>f</sup>	$b_1 \nu_{\text{N-N}}$
1796.3		[1795]	$a_1 \nu_{\text{N-O}}$
		[1792]	
1749.4		[1750]	$b_2 \nu_{\text{N-O}}$
		[1748]	
Force Constants			
	$\text{Fe}(\text{CO})_2(\text{NO})_2^g$	$\text{Fe}(\text{CO})(\text{N}_2)(\text{NO})_2^g$	$\text{Fe}(\text{N}_2)_2(\text{NO})_2^g$
$k_{\text{NN}}$		2104	2071
$k_{\text{N}_2, \text{N}_2}$			21
$k_{\text{CO}}$	1718.7	1694	
$k_{\text{CO}, \text{CO}}$	40.9		
$k_{\text{NO}}$	1418.9	1401	1385
$k_{\text{NO}, \text{NO}}$	33.2	34	36

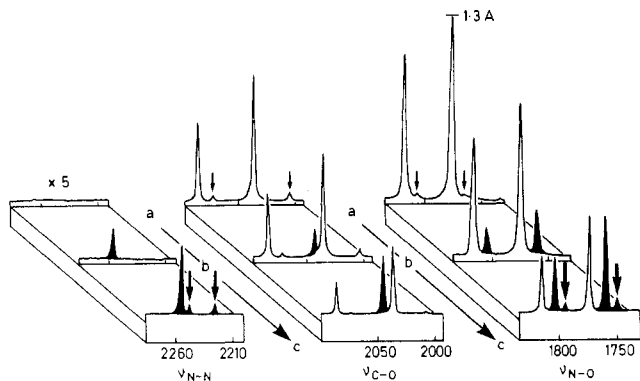
<sup>a</sup> Calculated by using the force constants tabulated below. Force constants were optimized with a "least-squares" refinement.<sup>7</sup> A more complete force constant analysis has been performed by Poletti et al.<sup>5</sup> <sup>b</sup> Taken from ref 4; bands assigned to matrix splittings bracketed together. <sup>c</sup> On the basis of  $C_{2v}$  symmetries for  $\text{Fe}(\text{CO})_2(\text{NO})_2$  and  $\text{Fe}(\text{N}_2)_2(\text{NO})_2$  and  $C_s$  symmetry for  $\text{Fe}(\text{CO})(\text{N}_2)(\text{NO})_2$ . <sup>d</sup> Natural-abundance  $^{13}\text{C}$  and  $^{15}\text{N}$ . <sup>e</sup>  $\nu^{12}\text{C-O} - \nu^{13}\text{C-O} = 45.0 \text{ cm}^{-1}$  (observed),  $45.6 \text{ cm}^{-1}$  (predicted). <sup>f</sup> Exact matrix band positions are uncertain because of the weakness of the bands. <sup>g</sup> Calculated assuming no vibrational coupling between N-N, C-O, and N-O groups.

$\text{Ni}(\text{CO})_4$ ) of unstable species. There has long been interest<sup>3</sup> in the kinetics of ligand substitution in the isoelectronic series  $\text{Ni}(\text{CO})_4$ ,  $\text{Co}(\text{CO})_3\text{NO}$ , and  $\text{Fe}(\text{CO})_2(\text{NO})_2$ . It therefore seemed appropriate in light of our  $\text{Ni}(\text{CO})_3\text{N}_2$  experiments<sup>2</sup> to investigate the generation and thermal stability of  $\text{Fe}(\text{C-O})(\text{N}_2)(\text{NO})_2$  and  $\text{Fe}(\text{N}_2)_2(\text{NO})_2$ , particularly as Crichton and Rest have identified these presumably unstable species by photolysis of  $\text{Fe}(\text{CO})_2(\text{NO})_2$  in solid  $\text{N}_2$  matrices<sup>4</sup> at 10 K. This note summarizes our results.

Figure 1 shows IR spectra illustrating the photolysis of  $\text{Fe}(\text{CO})_2(\text{NO})_2$  dissolved in liquefied Krypton doped with 2%  $\text{N}_2$ . Initially (spectrum a), there are no bands in the N-N

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(2) Turner, J. J.; Simpson, M. B.; Poliakoff, M.; Maier, W. B., II. *J. Mol. Struct.* 1982, 80, 83; *J. Am. Chem. Soc.* 1983, 105, 3898.  
 (3) Basolo, F. *Inorg. Chim. Acta* 1981, 50, 65.  
 (4) Crichton, O.; Rest, A. J. *J. Chem. Soc., Dalton Trans.* 1977, 656.  
 (5) Poletti, A.; Santucci, A.; Foffani, A. *J. Mol. Struct.* 1969, 3, 311.



**Figure 1.** IR spectra of  $\text{Fe}(\text{CO})_2(\text{NO})_2$  and photoproducts in liquid Kr doped with 2%  $\text{N}_2$  at  $-155^\circ\text{C}$ . The spectra are plotted in absorbance, and the N-N region is expanded  $\times 5$ : (a) prior to photolysis, arrowed peaks due to natural-abundance  $^{13}\text{C}$  and  $^{15}\text{N}$  (see table); (b) after 4-min UV photolysis, black bands due to  $\text{Fe}(\text{CO})(\text{N}_2)(\text{NO})_2$ ; (c) after a further 66-min photolysis, arrowed bands due to  $\text{Fe}(\text{N}_2)_2(\text{NO})_2$ .

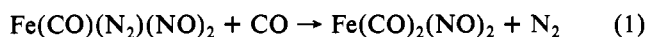
stretching region and two strong bands in both the C-O and N-O stretching regions, at wavenumbers close to those of matrix-isolated  $\text{Fe}(\text{CO})_2(\text{NO})_2$  but without the matrix splittings (see Table I). There are also four weak bands (arrowed) due to naturally occurring  $^{13}\text{C}$  (1.1%) and  $^{15}\text{N}$  (0.35%). Table I gives the force constants calculated for a simple energy-factored force field, which ignores any coupling between C-O and N-O vibrations. The good agreement between experimental and calculated frequencies confirms this apparent independence of the CO and NO vibrators. After 4 min of UV photolysis (spectrum b), the bands due to  $\text{Fe}(\text{CO})_2(\text{NO})_2$  have decreased, and one new band has appeared in the  $\nu_{\text{N-N}}$  region, one has appeared in the  $\nu_{\text{C-O}}$  region, and two new bands have appeared in the  $\nu_{\text{N-O}}$  region. These bands, colored black in spectrum b, are close in frequency to those of matrix-isolated<sup>4</sup>  $\text{Fe}(\text{CO})(\text{N}_2)(\text{NO})_2$  and can be assigned unambiguously to this molecule (see Table I).

Further UV photolysis (spectrum c) decreases the concentration of  $\text{Fe}(\text{CO})_2(\text{NO})_2$ , increases the concentration of the primary photoproduct  $\text{Fe}(\text{CO})(\text{N}_2)(\text{NO})_2$ , and generates a third species with two N-N bands, no C-O bands, and two N-O bands (arrowed). These bands are clearly due to  $\text{Fe}(\text{N}_2)_2(\text{NO})_2$  and are compared in the table with the matrix data.<sup>4</sup> There was difficulty in detecting any N-N stretching bands for this molecule in the matrix<sup>4</sup> because they were weak, and this may explain the larger difference in frequency for these bands between liquid Kr solution and matrix. Thus, our experiments show that UV photolysis of  $\text{Fe}(\text{CO})_2(\text{NO})_2$  in liquid Kr leads to stepwise substitution of the CO groups, just as it did in the matrix.<sup>4</sup>

$\text{Ni}(\text{CO})_3\text{N}_2$ , generated by photolysis of  $\text{Ni}(\text{CO})_4$  in liquefied Kr/ $\text{N}_2$ , reacts rapidly<sup>2</sup> with CO ( $t_{1/2} \sim 1/2$  min at  $-155^\circ\text{C}$ ). At the same temperature  $\text{Fe}(\text{N}_2)_2(\text{NO})_2$  disappears ( $t_{1/2} \sim 40$  min), presumably to form  $\text{Fe}(\text{CO})(\text{N}_2)(\text{NO})_2$ , although unfortunately the expected growth in the bands of  $\text{Fe}(\text{CO})(\text{N}_2)(\text{NO})_2$  could not be established with certainty in our experiment. Even allowing for the difference in CO concentrations between the Ni and Fe experiments, it is clear that, at  $-155^\circ\text{C}$ ,  $\text{Fe}(\text{N}_2)_2(\text{NO})_2$  is considerably less reactive toward CO than  $\text{Ni}(\text{CO})_3(\text{N}_2)$ .

By contrast, the primary photoproduct  $\text{Fe}(\text{N}_2)(\text{CO})(\text{NO})_2$  is almost completely stable at  $-155^\circ\text{C}$  and only begins to disappear as the temperature of the solution is raised. Warming the solution from  $-155$  to  $-107^\circ\text{C}$  over 2 h led to a  $\sim 50\%$  decrease in the intensity of the  $\text{Fe}(\text{CO})(\text{N}_2)(\text{NO})_2$  bands with a corresponding increase in the bands due to  $\text{Fe}(\text{CO})_2(\text{NO})_2$  confirming that reaction 1 is occurring. Thus,  $\text{Fe}(\text{CO})(\text{N}_2)(\text{NO})_2$  is very much less reactive toward CO than

is  $\text{Ni}(\text{CO})_3(\text{N}_2)$ , which is not surprising.<sup>3</sup>



This experiment again demonstrates the value of liquefied noble-gas solvents. We can now establish the thermal stabilities of unstable molecules, previously only observed in solid matrices at very low temperatures, and the thermal chemistry of a whole new class of compounds is accessible.

### Experimental Section

The high-pressure/low-temperature IR cell (2.7-cm path length; 8.5-mL volume) has been described previously.<sup>1,2</sup> Krypton and  $\text{N}_2$  (BOC research grade) were used without further purification.  $\text{Fe}(\text{CO})_2(\text{NO})_2$  was prepared by published methods.<sup>6</sup> All spectra were recorded with a Nicolet MX-3600 FTIR interferometer using 32K data points ( $0.7\text{-cm}^{-1}$  resolution), 3 degrees of zero filling, and Happ-Genzel Apodization in the Fourier transform, and 100 scans were performed for each data collection. The UV photolysis source was Phillips 25-W Cd lamp.

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**Registry No.**  $\text{Fe}(\text{CO})_2(\text{NO})_2$ , 13682-74-1;  $\text{Fe}(\text{CO})(\text{N}_2)(\text{NO})_2$ , 63576-04-5;  $\text{Fe}(\text{N}_2)_2(\text{NO})_2$ , 63576-05-6; Kr, 7439-90-9;  $\text{N}_2$ , 7727-37-9.

(6) See e.g., "Organometallic Synthesis"; Eisch, J. J., King, R. B., Eds.; Academic Press: London, 1965; Vol. 1.

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### Reactivity of a Bridging Sulfhydryl Ligand, S-Alkylation of $[\text{Mo}(\text{NC}_6\text{H}_4\text{CH}_3)(\text{S}_2\text{P}(\text{OC}_2\text{H}_5)_2)_2(\mu\text{-S})(\mu\text{-SH})(\mu\text{-O}_2\text{CCF}_3)]_2$ , and Structure of $[\text{Mo}(\text{NC}_6\text{H}_4\text{CH}_3)(\text{S}_2\text{P}(\text{OC}_2\text{H}_5)_2)_2(\mu\text{-S})(\mu\text{-SCH}_3)(\mu\text{-O}_2\text{CCF}_3)]_2$

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An increased attention to ligated sulfhydryl groups may be traced in part to an awakening interest in hydrodesulfurization (HDS) during the refinement of petroleum. The appearance of this ligand on the surface of a laboratory catalyst for HDS after the chemisorption of molecular hydrogen suggests that the ligand is also formed during HDS over the similar commercial catalyst.<sup>1</sup>

Nucleophilic properties resembling those of a thiol appear to be characteristic of terminal and most bridging sulfhydryl ligands. For example, the bridging ligands in  $[\text{Fe}(\text{CO})_3(\mu\text{-SH})_2]$  can be alkylated with either alkyl halides or activated alkenes.<sup>2</sup> The properties of the bridging sulfhydryl ligands in  $[(\eta^5\text{-C}_5\text{H}_4\text{CH}_3)\text{Mo}(\mu\text{-S})(\mu\text{-SH})_2]$ , however, appear to be unique. Unlike a thiol, this compound reacts with ethylene and does so with the formation of two bridging 1,2-dithiolates and the elimination of  $\text{H}_2$ .<sup>3</sup> The relatively high formal ox-

(1) The chemisorption of molecular hydrogen by  $\text{MoS}_2$  results in ligated SH groups as shown by: Badger, E. H. M.; Friggith, R. H.; Newling, W. S. B. *Proc. R. Soc. London Ser. A* **1949**, *197*, 184. The catalytic properties of  $\text{MoS}_2$  during hydrodesulfurization have been likened to those of the industrial catalyst by: Kolberg, S.; Amberg, C. H. *Can. J. Chem.* **1966**, *44*, 2623.

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