of the Hebrew University for his critical reading of the manuscript.

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Communications to the Editor

cis-Methyldiazene

Sir:

cis-Diazene (diimide) has been implicated as an intermediate in stereospecific reductions by in situ generated diazene[1] and in nitrogenase action on nitrogen.[2] This molecule and its rather well-studied trans isomer[3,4] have been the objects of a number of theoretical studies.[5] Yet, only fragmentary and inconclusive evidence has been reported for the direct observation of the cis isomer.[6,7] We now report the isolation of the closest homologue of *cis*-diazene, *cis*-methyldiazene, and its infrared spectrum. Based on the assignment of this spectrum, we conclude that *cis*-diazene is yet to be observed.

Hutton and Steel obtained *cis*-dimethyldiazene by photolysis of solid *trans*-dimethyldiazene with near-UV light at liquid nitrogen temperature.[8] A similar experiment with *trans*-$CH_3N{=}ND$[9] has given a new substance that has properties appropriate to *cis*-$CH_3N{=}ND$. Approximately 0.5 mmol of the trans isomer were distilled onto a CsI crystal which was held at −196 °C in a conventional low-temperature infrared cell. Prior to photolysis the glassy deposit was annealed into polycrystalline material. Photolysis was carried out for 6 h with illumination from a 45-W, low-pressure mercury lamp. New infrared absorption bands appeared at 2180, 1560, and 1060 cm^{-1}. The bands due to *trans*-$CH_3N{=}ND$ had decreased in intensity and had reverted toward the structureless appearance of glassy material. After the deposit was annealed again, the new features were seen more clearly and a small amount of noncondensible gas, presumably nitrogen, was pumped from the cell. Cautious cycling of the temperature between −196 °C and values progressing through the range of −125 to −113 °C, as well as repeated evacuation of the cell (at −196 °C), caused the relatively large amount of unconverted *trans*-$CH_3N{=}ND$ to sublime from the CsI plate to the surfaces of the surrounding copper support and liquid nitrogen well. The large difference in volatility between the two isomers of methyldiazene is consistent with the boiling point difference of nearly 100 °C found for *cis*- and *trans*-dimethyldiazenes.[10]

Figure 1 gives the infrared spectrum of the residual deposit. Table I gives the vibrational assignment for *cis*-$CH_3N{=}ND$ in comparison with that of the trans isomer.[9] That many of the frequencies of the fundamentals of this molecule are nearly coincident with those of the trans isomer is reasonable and is supported by zero-order normal coordinate calculations.[11] Bands are present for methyl group stretching and bending, for N=N stretching, and for ND stretching and bending. The band due to N=N stretching is a much more intense feature of this spectrum than in that of the trans isomer. The largest frequency shift, a decrease of ~120 cm^{-1}, occurs in the ND stretching mode. Two satellite bands in the spectrum are attributed to hydrogen bonding. Several features are due to *cis*-$CH_3N{=}NH$ which was formed from the isotopic impurity present in the trans isomer.

Several other possible products of the photolysis were considered but discarded. These included CH_3D, CH_3CH_3, *trans*-$DN{=}ND$, and *trans*-$HN{=}ND$, for which published spectra were available. Furthermore, these substances should have vaporized during the temperature cycling. The hydrazone of methyldiazene-d_1, $CH_2{=}NNHD$, which is a possible rearrangement product, does not fit the observed spectrum. This molecule has no methyl group and would have a C=N

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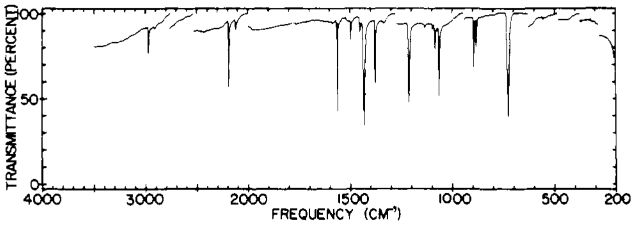

Figure 1. Infrared spectrum of polycrystalline *cis*-methyldiazene at −196 °C.

stretching frequency near 1600 cm^{-1}, NH stretching above 3100 cm^{-1}, and CH stretching above 3000 cm^{-1}.[10]

As a further test of the identification of the new material as *cis*-$CH_3N{=}ND$, it was photolyzed again without changing the temperature from −196 °C. After photolysis for 1 h, bands due to the trans isomer were evident, especially in the ND stretching region between 2320 and 2250 cm^{-1}. Photolysis for a second hour caused an increase in the intensity of the bands attributable to the trans isomer. After an annealing cycle, bands due to the trans isomer were even more apparent.

The same sequence of experiments, including the rephotolysis step, was performed on *trans*-$CD_3N{=}ND$ with comparable results. However, when *trans*-$CH_3N{=}NH$ was tried, we were unsuccessful in isolating the cis isomer even though bands attributable to this species were observed after photolyzing and annealing the solid. As the temperature was cycled upward above −120 °C, the intensity of the cis band at 1570 cm^{-1} decreased along with the intensity of the neighboring trans band. All bands were gone after the −113 °C cycle. Thus, it appears that a narrow temperature range exists in which the kinetic isotope effect gives the ND-containing cis molecule sufficient additional stability to remain intact, while the much more volatile trans isomer sublimes. In the experiments with *cis*-$CH_3N{=}ND$, it was finally lost from the CsI crystal at −100 °C.

The marked decrease in the ND stretching frequency in going from *trans*-methyldiazene to *cis*-methyldiazene is consistent with a correlation to which McKean[12] and Bellamy and Mayo[13] have drawn attention. These investigators have shown that a CH, NH, or OH bond that is oriented trans to an unshared electron pair on a neighboring atom has a significantly decreased vibrational frequency. This effect correlates with a weakened XH bond owing to interaction between the orbital of the unshared electron pair and the antibonding orbital of the XH bond. *cis*-Methyldiazene and *cis*-diazene have the requisite geometry for this effect; the trans isomers do not.

Normal coordinate calculations for *cis*-diazene-d_0 and -d_2 gave 2994 and 2956 cm^{-1} and 2195 and 2150 cm^{-1} for NH and ND stretching frequencies, respectively.[14] Reasonable changes in force constants other than the one for NH(D) stretching, which had been fit to *cis*-methyldiazene-d_1 and -d_4, did not cause significant changes in the frequencies of interest here. In view of these predicted frequencies, it is doubtful that *cis*-diazene has been observed to date. Rosengren and Pimentel assigned an infrared band at 3074 cm^{-1} to *cis*-diazene as one of several products of the photolysis of matrix-isolated hydrazoic acid.[6] However, the highest fundamental frequency for *cis*-diazene should be <3000 cm^{-1}. Wiberg, Fischer, and Bachhuber thermally decomposed potassium tosylhydrazide and its deuterated analogue.[7] *trans*-Diazene is a confirmed product of the thermal decomposition of the sodium salt.[3b] They obtained infrared spectra of condensates which were interpreted as due to a mixture of the cis and trans isomers of diazene-d_0 and to pure *cis*-diazene-d_2; 3116 and 3025 cm^{-1} were assigned to the d_0 species, and 2305 and 2275 cm^{-1} to the d_2 species. Both sets of frequencies appear to be too high,[15] and the splitting in the d_0 set is clearly too large. Owing to effects of crystal splitting, hydrogen bonding, and decomposition products, many possibilities exist for extraneous bands in this system. Also, given the low volatility and marked instability of *cis*-methyldiazene, it is doubtful that *cis*-diazene can be distilled in a vacuum system as was necessary in this latter experiment.

Table I. Infrared Spectra of *cis*- and *trans*-$CH_3N{=}ND$

cis isomer		trans isomer[a]		assignment		
freq, cm^{-1}	int[b]	freq, cm^{-1}	int[b]		approx description[c]	sym species
2975	w	2976	sh	ν_1	a$\nu(CH_3)$	a′
2972	m	2973	m	ν_{11}	a$\nu(CH_3)$	a″
2915	vw	2908	m	ν_2	s$\nu(CH_3)$	a′
2188	ms	2317	ms	ν_3	ν(ND)	a′
2124	vw	2264	s	H bonded	ν(ND)	
2119	w					
1571	w	1562	w	ν_4	$CH_3N{=}NH$	
1565	s	1559	m	ν_4	ν(NN)	a′
1499	m	1509	m	H bonded	$CH_3N{=}NH$	
1456	w	1469	w	ν_5	$CH_3N{=}NH$	
1437	s	1434	s	ν_5	$\delta(CH_3)$	a′
1433	s	1424	s	ν_{12}	$\delta(CH_3)$	a″
1382	ms	1380	ms	ν_6	$\delta(CH_3)$	a′
1379	ms	1375				
		1220	m	H bonded	δ(ND)	
1216	s	1212	m	ν_7	δ(ND)	a′
1102	w				$CH_3N{=}NH$?	
1088	m	1089	m	ν_{13}	$\rho(CH_3)$	a″
1067	s	1077	m	ν_8	$\rho(CH_3)$	a′
898	m	890	ms	ν_9	ν(CN)	a′
884	mw	886	sh	H bonded	$CH_3N{=}NH$	
718	s, br	715	ms	H bonded	β(ND)	a″
		666[d]	s	ν_{14}	β(ND)	a″
560	vw	556	s	ν_{10}	δ(CNN)	a′

[a] Reference 2b. [b] w = weak, m = medium, s = strong, v = very, sh = shoulder, br = broad. [c] ν = stretch, δ = bend, ρ = rock, β = out of plane bend, s = symmetric, a = antisymmetric. [d] From spectrum of dilute matrix in nitrogen.

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1019 (1973); D. Sellmann, *ibid.*, **13**, 639 (1974). In the infrared spectrum of the complex, $N_2H_2[Cr(CO)_5]_2$, the N_2H_2 bridging ligand is assigned a cis configuration. NH stretching frequencies of 3480 and 3250 cm^{-1} are observed. These frequencies are not in conflict with the present results for *cis*-methyldiazene and the predictions for *cis*-diazene, since complexation engages the unshared electron pairs in bonding and modifies the strengths of the bonds in the *cis*-diazene ligand.

Norman C. Craig,* Mark A. Kliewer, Nancy C. Shih
Department of Chemistry, Oberlin College
Oberlin, Ohio 44074

Received August 18, 1978

Sulfur 2p Photoelectron Spectra of 1,8-Bis(2′-pyridyl)-3,6-dithiaoctane and Its Copper(II) Complex. Possible Interpretation of the S_{2p} 168-eV Peak in Blue Copper Proteins

Sir:

X-ray photoelectron spectroscopy (XPES) could provide a simple, direct method of determining sulfur-copper coordination in metalloproteins. In principle, if a shift in the S_{2p} peak in the spectrum of the apoprotein from the same peak in the spectrum of the copper protein could be detected, then, qualitatively at least, sulfur-copper coordination would be implicated. Such studies have been reported on the blue protein, plastocyanin,[1] and on oxyhemocyanin.[2] The plastocyanin study suggested that a 4–5-eV shift in the S_{2p} peak occurred upon sulfur–copper coordination (from 164 to 168–169 eV) and, since only a major signal at 164 eV was observed for oxyhemocyanin, it was assumed that there is no sulfur-copper coordination in this protein.

Experience suggests that a 4-eV shift in the S_{2p} peak upon copper coordination is unreasonably large, since the energy of the S_{2p} peak seems to be largely determined by the formal oxidation state of the sulfur atom, spanning only 7 eV in transferring from S^{2-} to $SO_4{}^{2-}$.[3] Similar observations have been made before on a number of occasions,[4-7] and one group has proposed[6] that the 168-eV S_{2p} peak in the plastocyanin spectrum is due to $SO_4{}^{2-}$ or some other oxidized sulfur impurity. However, careful examination of the experimental facts has shown[2] that the 168-eV S_{2p} signal is a property of Co(II) or Cu(II) binding to apoplastocyanin. Clearly, the exact origin of the plastocyanin 168-eV S_{2p} signal must be elucidated if further XPS studies on proteins are contemplated.

The purpose of this communication is to describe an XPES study of the ligand 1,8-bis(2′-pyridyl)-3,6-dithiaoctane and its copper(II) complex[7] (Figure 1), where we show that a high energy S_{2p} binding peak (~168 eV) can be generated in the copper complex but that it is caused by copper-catalyzed radiation damage.

A comparison of the S_{2p} signal of the free ligand and its copper(II) complex obtained under normal conditions (~20-min X-ray exposure at 25 °C) is shown in Figure 1A, B. Clearly, no significant shift of the S_{2p} binding energy upon metal coordination is observed. However, a broad shoulder in the region 167–169 eV can be distinguished in Figure 1B that is not present in 1A. Since this shoulder is in precisely the region where the high energy binding peak of plastocyanin was observed, it was important to determine its origin.

Exposure of the complex to the X-ray source for 12 h gave the spectrum shown in Figure 1C. As can be seen, this exposure causes a dramatic increase in the intensity of the high-energy binding peak. The sample is visibly damaged after this treatment. Importantly, similar exposure of the free ligand did *not* give a high-energy binding peak. Finally, a 30-s exposure of the complex to an argon-ion etching beam causes complete changeover of the 164-eV peak to the one at 168 eV (Figure 1D). Again, no such effect is observed for the uncomplexed ligand.

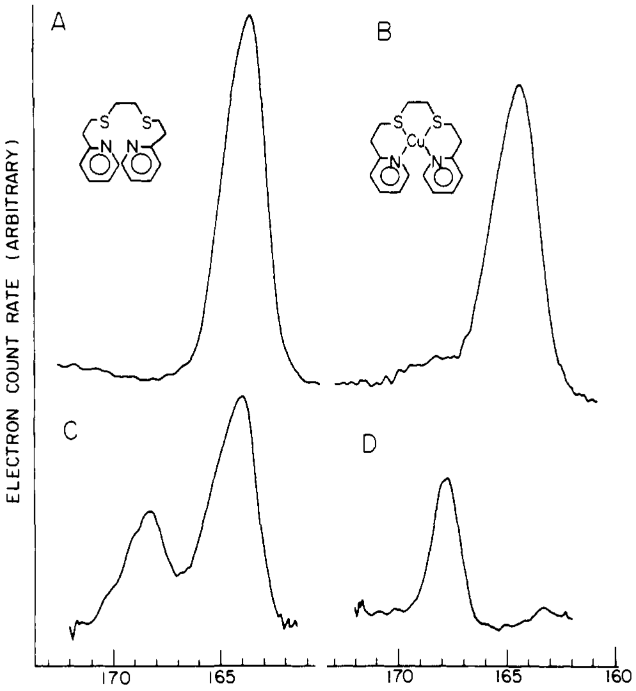

Figure 1. XP S_{2p} spectra of ligand (A), copper complex (B), after 12-h exposure to source beam (C), and complex after 10-s exposure to a 10-μA argon-ion beam. Samples were run on a McPherson ESCA 36 X-ray photoelectron spectrometer in the Mg Kα (250 W) mode.

It is clear from these results that very little shift of the S_{2p} binding peak occurs upon copper coordination to sulfur and that the higher energy peak arises from other sources. The position of the 168-eV peak corresponds to a sulfur atom at the oxidation level of a sulfone,[3] which implies that radiation-induced surface oxidation has occurred, but, as we have shown, this oxidation occurs *only in the presence of ligated copper*, an observation that bears directly on attempts to correlate the results obtained for apo- and metalloproteins.

The high binding peak (168 eV) observed in plastocyanin and in other blue proteins[2] could be due to the effect described here[9] or it could possibly be a charge-transfer satellite, as proposed by Larsson.[10] Measurements of S_{2s} binding energies are being made on several blue protein samples in an attempt to resolve the issue.[11] It also should be emphasized that the absence of a pronounced high-energy S_{2p} peak in the oxyhemocyanin spectrum[2] does not conclusively rule out sulfur ligation, as there are ~20 sulfur atoms per copper pair in these proteins,[12] and it would be difficult to see a signal attributable to only a few of these. In view of the latter comment, as well as the uncertainty in the interpretation of the 168-eV S_{2p} peak in plastocyanin, it is our opinion that it would be unwise to infer copper-sulfur coordination in proteins based solely on XPE spectroscopic measurements.

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