

and to the production of three new nucleosidic derivatives which might be located by the cysteine spray reagent. The two nucleosides, which have an α -diol group,¹⁰ have been shown to be respectively 1-(2-deoxy- β -D-erythro-pentopyranosyl)thymine (7) and 1-(2-deoxy- α -D-erythro-pentopyranosyl)thymine (8). The last nucleosidic compound has been identified as 1-(2-deoxy- α -D-erythro-pentafuranosyl)thymine (6).

The acid solvolysis of 0.1 M 2'-deoxyuridine produced similar corresponding compounds, *i.e.*, 1-(2-deoxy- α -D-erythro-pentofuranosyl)uracil (9), 1-(2-deoxy- β -D-erythro-pentopyranosyl)uracil (10), 1-(2-deoxy- α -D-erythro-pentopyranosyl)uracil (11), and uracil (12). All these nucleosides have been characterized by ir, uv, CD, mass spectrometry, and by comparison with authentic samples.^{11,12}

On the other hand, the acid hydrolysis of 5-bromo-2'-deoxyuridine and of 2'-deoxycytidine gave only the rupture of the *N*-glycosidic bond.

The quantitative importance of the rearrangement and of the cleavage reactions has been measured and is shown in Table I.

The electronic shifts (pathway A) from the pyrimidic moiety to the annular oxygen were important, and it is worth noting that the yield of the isomerization decreased in the expected order, thymidine > 2'-deoxyuridine > 5-bromo-2'-deoxyuridine.¹³ Hydrolysis of the acyclic Schiff base partially explained the release of thymine and uracil.

In conclusion, different mechanisms (A_1 mechanism, C-O rupture) as previously suggested by Capon^{4b} may be involved in the nucleosidic acid hydrolysis.

Acknowledgments. The authors are indebted to Mrs. Georges and Miss Pouchot for their skillful assistance throughout this work.

(10) The periodic oxidation of the two nucleosides gave corresponding "dialdehydic nucleosides."

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(12) J. Cadet, *Tetrahedron Lett.*, 867 (1974); J. Cadet and R. Teoule, *Carbohydr. Res.*, **29**, 345 (1973); H. Quelo, J. Cadet, and R. Teoule, *C. R. Acad. Sci., Ser. C*, 275, 1137 (1972); J. Ulrich, J. Cadet, and R. Teoule, *Org. Mass Spectrom.*, **7**, 543 (1973).

(13) The easier ring oxygen isomerization of the 5-bromo-6-hydroxy-5,6-dihydrothymidine and of the 5,5-dibromo-6-hydroxy-5,6-dihydro-2'-deoxyuridine¹² in acidic medium was correlated with the increase of the basicity of N_1 atom.

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Addition of Nitrosonium Ion to Mercaptide-Bridged Binuclear Iron(II) and Cobalt(II) Complexes

Sir:

The mercaptide-bridged iron(II) dimer of *N,N'*-dimethyl-*N,N'*-bis(β -mercaptoethyl)ethylenediamine, $(FeL)_2$ (1), has been shown to have a distorted geometry with a short nonbonded Fe \cdots Fe distance of 3.206 (5) Å attributable to local constraints.¹ This compound

(1) W. J. Hu and S. J. Lippard *J. Amer. Chem. Soc.*, **96**, 2366 (1974).

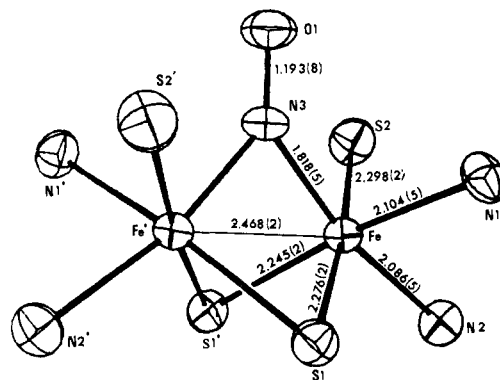
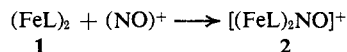


Figure 1. The inner coordination sphere of $[(FeL)_2NO]PF_6 \cdot$ acetone showing the 40% probability thermal ellipsoids. Selected bond angles are (deg): Fe-N3-Fe', 85.5 (3); Fe-N3-O1, 137.2 (1); Fe-S1-Fe', 66.2 (1); N3-Fe-S1, 90.6 (1); N3-Fe-S1', 91.6 (1); S1-Fe-S1', 80.6 (1); S1-Fe-N1, 84.8 (1); N1-Fe-N2, 84.6 (2); N2-Fe-S2, 84.3 (1); N3-Fe-N2, 168.5 (2); N1-Fe-S1', 165.3 (1); S1-Fe-S2, 175.3 (1).

is highly reactive. Here we report its reaction with nitrosonium salts to form the novel nitrosyl bridged dimeric cation 2.



Addition of methylene chloride under nitrogen to a solid mixture of 1 and either $(NO)PF_6$ or $(NO)BF_4$ produced a dark brown solution containing 2. Purification was effected by fractional crystallization from CH_2Cl_2 -EtOAc.^{2,3} The infrared spectrum of 2 (Nujol mull) shows a peak of medium intensity at 1553 cm^{-1} which may be assigned to the stretching vibration of a bridging nitrosyl ligand.⁴ The 77°K Mössbauer effect spectrum of the BF_4^- salt of 2 exhibits a single quadrupole split doublet with $\delta = 0.29\text{ mm/sec}$ relative to natural iron foil and $\Delta E_Q = 1.54\text{ mm/sec}$, consistent with chemically equivalent iron atoms. Thus the nitrosonium cation adds to the mercaptide-bridged bimetallic center in 1 and now bridges the two iron atoms.

This interpretation has been confirmed by a single-crystal X-ray structure determination. Crystals of $[(FeL)_2NO]PF_6 \cdot$ acetone, obtained upon recrystallization from acetone-ethanol, belong to the orthorhombic space group $Ama2-C_{2v}^{16}$ with cell dimensions $a = 24.18$ (2) Å, $b = 15.670$ (7) Å, $c = 8.011$ (4) Å, $\rho_{obsd} = 1.66$ (2) g/cm^3 , $\rho_{calcd} = 1.657\text{ g/cm}^3$ for four formula units per unit cell. The structure was solved by the heavy atom method using 1345 independent reflections ($2\theta < 55^\circ$, $F^2 > 3\sigma(F^2)$) collected on a four-circle automated diffractometer using monochromatized Mo $K\alpha$ radiation. Refinement by full-matrix least-squares methods yielded final values for the usual agreement factors $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$ and $R_2 = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}$ of 0.032 and 0.037, respectively. During refinement the acetone molecule was treated as a rigid

(2) *Anal.* (Galbraith Laboratories) Calcd for $C_{16}H_{18}N_8S_4OPF_6Fe_2$: C, 27.47; H, 5.19; N, 10.01; S, 18.34; F, 16.30; P, 4.43. Found: C, 27.20; H, 5.06; N, 9.80; S, 18.20; F, 16.12; P, 4.30. Calcd for $C_{16}H_{18}N_8S_4OBF_4Fe_2$: C, 29.97; H, 5.65; N, 10.92; S, 20.00; B, 1.69. Found: C, 29.60; H, 5.65; N, 10.20; S, 19.17; B, 1.78.

(3) The complex 2 is also produced in high yield using nitronium salts, *e.g.*, $(NO_2)PF_6$, instead of nitrosonium salts (*cf.* A. N. Nesmeyanov, K. N. Anisimov, N. E. Kolobova, and L. L. Krasnoslobodskaya, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 860 (1970)).

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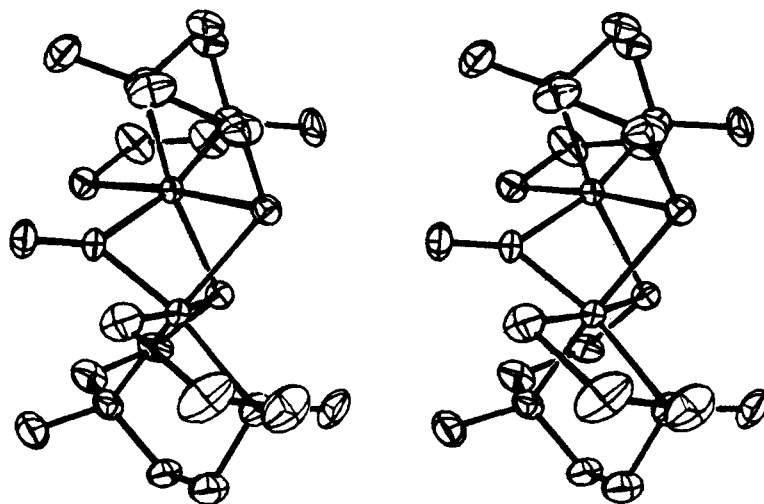


Figure 2. Stereoscopic view of the $[(\text{FeL})_2\text{NO}]\text{PF}_6 \cdot \text{acetone}$ complex cation. Thermal ellipsoids are at the 30% probability level and hydrogen atoms are omitted for clarity.

group, all other atom positional parameters were allowed to vary, nonhydrogen atoms were assigned anisotropic thermal parameters, and hydrogen atoms were assigned isotropic thermal parameters. The positional and thermal parameters as derived from the last cycle of least-squares refinement, a compilation of observed and calculated structure factor amplitudes, and tables of intramolecular bond distances and angles are available.⁵

As shown in Figures 1 and 2, the structure of the cation consists of two distorted iron octahedra sharing a common face comprised of two bridging mercaptide sulfur atoms and the nitrogen atom of the nitrosyl ligand. A crystallographically imposed twofold axis passes through the N–O bond, requiring the bridge geometry to be symmetric. The iron–iron separation of 2.468 (2) Å indicates the formation of a metal–metal single bond,^{6,7} which provides each iron atom in **2** with an 18-electron configuration. The iron nitrosyl geometry (Figure 1) is similar to that found in other known doubly-bridging nitrosyl metal complexes.^{7,8} The Fe–S and Fe–N bond lengths in low spin **2** (Figure 1) are shorter than the corresponding values¹ in high spin **1**. This reduction in bond length is accompanied by an increase in the intrachelate angle Ni–Fe–N2 toward a normal octahedral value, providing relief of the ligand constraints¹ in **1** that may help to drive the reaction of **1** → **2**.

Cyclic voltammetric measurements of **2** show a quasi-reversible one-electron wave with a cathodic to anodic current ratio of ~2.5 (acetonitrile, $E_{1/2} = -0.42$ V vs. sce).⁹ Continued cathodic scanning reveals further

reduction. Addition of tetraethylammonium borohydride to **2** in acetonitrile produces **1** which can be isolated in ~50% yield.

The cobalt(II) complex analogous to **1**, $(\text{CoL})_2$, has also been prepared^{10a} and found to be quite reactive. With nitrosonium salts this complex yields the $[(\text{CoL})_2\text{NO}]^+$ cation, judging from infrared ($\nu_{\text{NO}} = 1545 \text{ cm}^{-1}$) and analytical^{10b} data, and the observed diamagnetism.

The addition of NO^+ to the bimetallic iron center (**1** → **2**) may be compared with the oxidative addition reactions of coordinatively unsaturated d^8 complexes,^{11,12} since **1** contains two 16-electron iron(II) atoms that achieve an 18-electron configuration in the cation, **2**. In the case of cobalt, assuming no metal–metal bonding, $(\text{CoL})_2$ contains two 17-electron metal centers that attain an 18-electron configuration after addition of NO^+ to produce the $[(\text{CoL})_2\text{NO}]^+$ cation. The assumption that no metal–metal bond exists either in $(\text{CoL})_2$ or in $[(\text{CoL})_2\text{NO}]^+$ will be checked by X-ray structural studies.

The present study demonstrates that addition reactions to bimetallic iron(II) and cobalt(II) centers can occur with the nitrosonium cation. The reactions of other small molecule substrates with these compounds are currently under investigation.

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Supplementary Material Available. Tables I and II showing nonhydrogen and hydrogen atomic positional and thermal parameters, respectively, Tables III and IV showing internuclear bond angles and distances, and Table V reporting the observed and

(5) See paragraph at end of paper regarding supplementary material.

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(9) Measurements were conducted at sweep rates varying from 0.1 to 10 V/sec with 0.1 M tetra-*n*-butylammonium perchlorate as supporting electrolyte and a stationary platinum bead working electrode.

(10) (a) *Anal. Calcd for C₈H₁₈N₂S₂Co*: C, 36.22; H 6.84; N, 10.55; S, 24.17. Found: C, 36.18; H, 6.78; N, 10.28; S, 24.25; (b) *Anal. Calcd for C₁₆H₃₆N₄S₄OPF₆Co₂*: C, 27.24; H, 5.14; N, 9.92; S, 18.18; P, 4.39. Found: C, 27.28; H, 5.09; N, 9.56; S, 18.38; P, 4.32.

(11) (a) J. P. Collman, *Accounts Chem. Res.*, **1**, 136 (1968); (b) J. Halpern, *ibid.*, **3**, 386 (1970).

(12) The analogy is not rigorous, however, since the reaction of **1** with NO^+ to form **2** involves a high-spin to low-spin conversion.

calculated structure factor amplitudes for $[(\text{FeC}_5\text{H}_{18}\text{N}_2\text{S}_2)_2\text{NO}]\cdot\text{PF}_6\cdot\text{C}_9\text{H}_8\text{O}$ will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 \times 148 mm 24 \times reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St. N.W., Washington, D.C. 20036. Remit check or money order for \$4.00 for photocopy or \$2.00 for microfiche, referring to code number JACS-74-6519.

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Positional Dependence of the Heavy Atom Effect in the Cis-Trans Photoisomerization of Bromostilbenes¹

Sir:

Comparison of the temperature dependence of fluorescence, ϕ_f , and isomerization, $\phi_{t\rightarrow c}$ and $\phi_{c\rightarrow t}$, quantum yields for the stilbenes and the *p*-halostilbenes has revealed a substantial bromine substituent effect.²⁻⁵ Increasing the temperature in the parent hydrocarbon from -180 to 25° increases $\phi_{t\rightarrow c}$ while decreasing ϕ_f , these two processes being coupled throughout the temperature range.⁴⁻⁷ In *p*-bromostilbene $\phi_{t\rightarrow c}$ is reported to be temperature independent while ϕ_f increases modestly as the temperature is decreased.^{3,4} Bromine substitution brings into play an additional pathway for stilbene photoisomerization which is not activated and is generally assigned to heavy-atom-enhanced intersystem crossing.²⁻⁵ The temperature independence of $\phi_{c\rightarrow t}$ in the systems studied has revealed no difference in behavior between excited *cis*-stilbene and its halogen substituted derivatives.^{4,5} However, halogen substitution, especially in the meta position, has been reported to lower $\phi_{c\rightarrow t}$ significantly⁸ and it has been suggested that enhanced spin-orbit coupling induces very rapid $^1c \rightarrow ^3c \rightarrow ^0c$ decay.^{8,9} This suggestion contradicts the commonly expressed view that, with the exception of a minor cyclization component to dihydrophenanthrene, DHP, torsion about the central bond to twisted geometries, 1p and 3p , is the major decay mode of *cis* excited states.² In the following, observations are reported which allow a quantitative evaluation of triplet state involvement following direct excitation of the bromostilbenes.

Preliminary quantum yields obtained in our work¹⁰

(1) Presented in part at the Southeastern Regional Meeting of the American Chemical Society, Tallahassee, Fla., 1968, Abstract 113, and at the "Frontiers of Organic Photochemistry" Symposium sponsored by the New York Section of the American Chemical Society, Tarrytown, N. Y., 1970.²

(2) J. Saltiel, *et al.*, *Org. Photochem.*, **3**, 1 (1973).

(3) R. H. Dyck and D. S. McClure, *J. Chem. Phys.*, **36**, 2326 (1962).

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(7) J. Saltiel and J. T. D'Agostino, *J. Amer. Chem. Soc.*, **94**, 6445 (1972).

(8) K. Krüger and E. Lippert, *Z. Phys. Chem. (Frankfurt am Main)*, **66**, 293 (1969).

(9) E. Lippert, *Z. Phys. Chem. (Frankfurt am Main)*, **42**, 125 (1964).

(10) Irradiations were carried out in a merry-go-round apparatus.¹¹ Large *cis*-*trans* conversions due to bromine atom catalysis were avoided by including mossy zinc in the irradiation ampoules.¹² The benzophenone-sensitized photoisomerization of *cis*-1,3-pentadiene was used

Table I. Isomerization Quantum Yields and Photostationary Compositions^a

Compound	$\phi_{t\rightarrow c}$	$\phi_{c\rightarrow t}$	% [t] _s	% [t] _s ^b
Stilbene	0.52 (0.50)	0.33 (0.35)	8.3 (7)	52
<i>m</i> -Bromostilbene	0.53 (0.46)	0.33 (0.18)	11.4 (6)	59
<i>m,m'</i> -Dibromostilbene	0.57 (0.53)	0.22 (<0.05)	8.0 (~0)	69
<i>p</i> -Bromostilbene	0.54 (0.35)	0.4 (0.16)	11.0 (-)	62

^a Experiments were carried out in *n*-pentane at 30° , 313 nm. Values in parentheses are from ref 4 and 8, *n*-hexane, 25° , 313 nm.

^b Photostationary states are attained using 254-nm excitation.

are shown in Table I along with corresponding values reported by Krüger and Lippert.⁸ Our observations indicate a modest but significant decrease in $\phi_{c\rightarrow t}$ for *m,m'*-dibromostilbene but do not show the previously reported dramatic decrease.¹⁴ Furthermore, Table I shows the *trans*-stilbenes to be significant components in photostationary states obtained with 313-nm irradiation and more so when excitation is at 254 nm where *cis* and *trans* isomers have similar extinction coefficients (*e.g.*, for *m,m'*-dibromostilbene $\epsilon_c/\epsilon_t = 0.157$ and 1.67 at 313 and 254 nm, respectively).

Bromine's influence on spin-orbit coupling in the stilbenes can be inferred from measurements of stationary states for direct and sensitized photoisomerizations in the presence of azulene.^{15,16} In all cases ($[t]/[c]_s$) stationary ratios are found to be linearly dependent on azulene concentration. Slope/intercept ratios are shown in Table II. These results can be

Table II. Azulene Effects on Photoisomerization of Stilbenes in Pentane at 30° ^a

Compound	r_d^b, M^{-1}	r_s^c, M^{-1}	% [t] _s ^d
Stilbene	14	304	37.0
<i>m</i> -Bromostilbene	12	140	45.3
<i>m,m'</i> -Dibromostilbene	23	400	37.5
<i>p</i> -Bromostilbene	31	56	39.6

^a Similar observations have been made in benzene. ^b Slope/intercept ratios for direct excitation at 313 nm; similar results were obtained at 254 nm. ^c Slope/intercept ratios for benzophenone sensitization. ^d Photostationary states for benzophenone sensitization in the absence of azulene, % [t]_s = 100β.

accounted for by the mechanism shown in Scheme I, where ϕ_{01p} is the quantum yield for twisted singlet formation from 1c , ϕ_{is}^{1t} and ϕ_{is}^{1p} are intersystem crossing quantum yields from 1t and 1p , k_s and k_t are rate constants for azulene quenching of stilbene singlets and

for actinometry.¹³ Samples were irradiated with 313-nm light in the presence and in the absence of visible light absorbed by the DHP's. Analyses were by glpc and were corrected for back reaction.¹³

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(14) Preliminary evidence suggests that the decrease in $\phi_{c\rightarrow t}$ in *m,m'*-dibromostilbene may be due to the larger moments of inertia of the aryl groups which tend to favor cyclization to DHP over torsional $^1c \rightarrow ^1p$ displacement.

(15) J. Saltiel and E. D. Megarity, *J. Amer. Chem. Soc.*, **94**, 2742 (1972).

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