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LETTERS

Extended Diaryl Diselenide Radical Cations in Pentasil Zeolite Studied by EPR and Diffuse Reflectance Optical Spectroscopy

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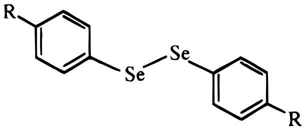
Incorporation of diaryl diselenides (1a, b; R = H, Cl) into pentasil zeolite generated "extended" selenium-centered radical cations (**1a**$^{\bullet+}$, **b**$^{\bullet+}$). These species are identified by their EPR ($g_{\mathrm{avg}} = 2.0644$, 2.0639) and diffuse reflectance spectra ($\lambda_{\mathrm{max}} = 520$, 550, 950 nm). The relative strength of the two-center three-electron Se−Se bond is compared with the corresponding S−S bond in diphenyl disulfide radical cation.

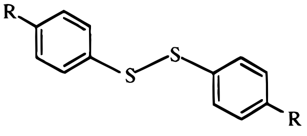
The structures and catalytic properties of zeolites have been extensively investigated as prototypes of acidic industrial catalysts.[1−3] In addition, various organic radical cations have been generated spontaneously by inclusion of appropriate precursors into zeolites.[4−7] Within the pores of the zeolite, the radical cations are protected from reagents that typically cause their decay in solution; accordingly, they have increased lifetimes and can be studied by conventional spectroscopic techniques. Furthermore, the limiting geometry of the zeolite pores may restrict the geometry of these intermediates. For example, only the fully extended conformers of *n*-hexane and *n*-octane radical cations were observed in pentasil zeolite following radiolysis.[8]

We are interested in intra-zeolite chemical reactions of radical cations. Recently, we found that σ-type neutral radicals, iminoxyls, could be generated from oximes, involving one-electron oxidation as well as deprotonation.[9] In addition, we have found evidence for oxidative dehydrogenation (formation of anethole radical cation from *p*-propyl anisole)[10] and oxidative cyclization with dehydrogenation (formation of thianthrenium radical cation, **3**$^{\bullet+}$; R = H) from the diphenyl disulfide radical cation (**2**$^{\bullet+}$; R = H).[11,12]

In view of the continuing interest in two-center three-electron σ- or π-bonds between pairs of sulfur atoms,[13−23] we have investigated radical cations containing the heavier congener, selenium. We adsorbed two diaryl diselenides (**1a**, **b**) as well as ditolyl disulfide (**2b**) onto the internal surface of a pentasil zeolite.[24,45] The resulting EPR and diffuse reflectance (DR) spectra[26] support diselenide radical cations, **1a**$^{\bullet+}$, **b**$^{\bullet+}$, which have not been observed previously. Because of the limiting geometry of the zeolite pores (either straight elliptical channels, 5.2 × 5.7 Å, or sinusoidal ones, with nearly circular diameter, ~5.5 Å) the observed species are most likely the extended conformers.



1a, R = H
1b, R = Cl



2a, R = H
2b, R = CH_3

Incorporation of the diselenides, (**1**; R = H, Cl), and of ditolyl

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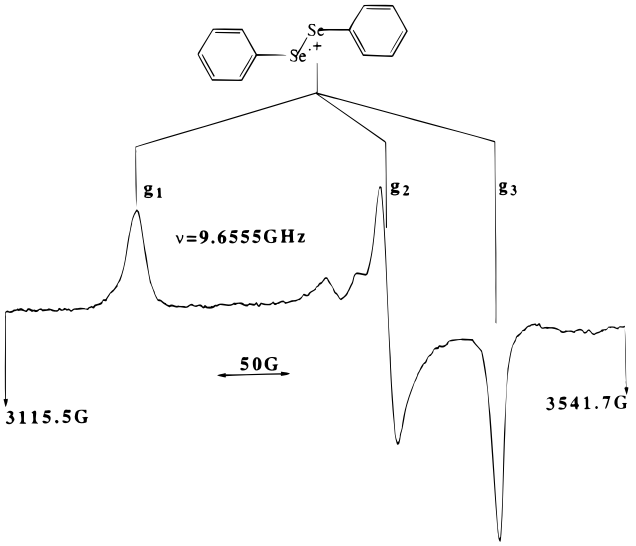


Figure 1. X-band EPR spectrum generated by incorporating diphenyl diselenide (**1a**) into the channels of a redox-active pentasil zeolite (Na-ZSM-5).[24] The powder pattern is identified as that of the radical cation, **1a**$^{\bullet+}$, with principal g values $g_1 = 2.1526$, $g_2 = 2.0425$, and $g_3 = 1.9982$; these values average to $g_{\mathrm{iso}} = 2.0644$.

TABLE 1. EPR Parameters of Radical Cations of Diaryl Dichalcogenides

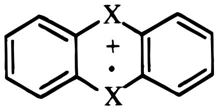
presursor	g_1	g_2	g_3	g_{ave}	ref
diphenyl disulfide	2.0263	2.0090	2.0022	2.0125	11,12
thianthrene	2.0136	2.0081	2.0024	2.0080	29
bis(*p*-tolyl) disulfide	2.0247	2.0095	2.0034	2.0125	this work
diphenyl diselenide	2.1526	2.0425	1.9982	2.0644	this work
bis(*p*-chlorophenyl) diselenide	2.1499	2.0422	1.9997	2.0639	this work

disulfide (**2**; R = CH_3) into a pentasil zeolite (Na-ZSM-5)[24,25] gave rise to EPR spectra with powder patterns characteristic for free radicals with unpaired spin density on “heavy” heteroatoms (Figure 1, 2). The spectrum obtained from **2b** has an orthorhombic powder pattern with $g_1 = 2.0247$, $g_2 = 2.0095$, and $g_3 = 2.0034$; the three principal g values average to $g_{\mathrm{avg}} = 2.0125$. The assignment of the spectrum obtained from **2b** rests on its similarity to that formed from **2a** ($g_1 = 2.0263$, $g_2 = 2.0090$, $g_3 = 2.0022$, $g_{\mathrm{avg}} = 2.0125$) and ascribed to the “extended” radical cation, **2a**$^{\bullet+}$ (Table 1).[11] Consequently, the intermediate is assigned structure **2b**$^{\bullet+}$.

Incorporation of diselenide **1a** resulted in a spectrum with $g_1 = 2.1526$, $g_2 = 2.0425$, and $g_3 = 1.9982$; the principal g values average to $g_{\mathrm{avg}} = 2.0644$. Similarly, **1b** generated a spectrum with $g_1 = 2.1499$, $g_2 = 2.0422$, and $g_3 = 1.9997$; $g_{\mathrm{avg}} = 2.0639$. The g components of the diselenide species, **1a**$^{\bullet+}$, **b**$^{\bullet+}$, are better resolved than are those of the disulfide species, **2a**$^{\bullet+}$, **b**$^{\bullet+}$, which have overlapping resonance lines for the two high field g components. Obviously, the higher congeners have a more pronounced g factor anisotropy.

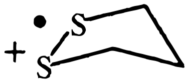
The g values of these radical cations are significantly greater than that of the selenanthrenium radical cation (**3**, X = Se; $g = 2.0315$).[27,28] This leads us to conclude that the diselenide radical cations do not undergo cyclization in the zeolite, in interesting contrast to the reaction of diphenyl disulfide radical cation (**2a**$^{\bullet+}$ → **3a**$^{\bullet+}$; X = S) both in solution[29] and in ZSM-5, particularly upon heating above 150°.[11,12]

Accordingly, the diselenide species are identified as “extended” radical cations, and assigned structures **1a**$^{\bullet+}$, **b**$^{\bullet+}$ (Table 1). The increased g values of the extended selenium and sulfur radical cations are ascribed to the formation of two-center-three-electron π-bonds between S−S and Se−Se;[13,14] the increased bond order (∼1.5 for **1**$^{\bullet+}$ and **2**$^{\bullet+}$ compared to 1.0 for **1** and **2**) causes the unpaired spin to be largely localized on the two heteroatoms; however, some delocalization into the aryl rings cannot be excluded.



3a$^{\bullet+}$

The extent of delocalization into the phenyl groups can be estimated for the sulfur species on the basis of a comparison of the g factors of **2a**$^{\bullet+}$ and of the 1,2-dithiolane radical cation,[30] **4**$^{\bullet+}$, both in the zeolite. The average g factor of **4**$^{\bullet+}$ (2.0172)[30] exceeds that of the free electron spin (2.0023) by 0.0149. This increase is ascribed to spin−orbit coupling from the sulfur centers. The corresponding g factor difference between **2a**$^{\bullet+}$ and the free electron spin (0.0102) is smaller by ∼30%. We conclude that the lower g factor corresponds to a lower electron spin density on sulfur and, correspondingly, to delocalization into the phenyl groups.



4$^{\bullet+}$

The spectra obtained from the diaryl diselenides (**1a**, **b**) are consistent with those of the disulfide radical cations, **2a**$^{\bullet+}$, **b**$^{\bullet+}$, once the significantly greater spin−orbit coupling of selenium compared to sulfur is taken into account. Stone proposed a linear relationship between the shift of the g factor from the free-spin value and the Hückel energy of the singly occupied p orbital for delocalized organic π-radicals,[31−33]

$$g - g_{\mathrm{e}} = b + c \times \lambda \tag{1}$$

where λ is the effective spin−orbit coupling constant, and b and c are constants.

The values of b and c may vary for different elements; for hydrocarbon radicals, the value of b is quite small, $b_{\mathrm{C}\pi} = 3.19 \times 10^{-4}$.[32] Assuming that c has similar values for the sulfur- and selenium-containing radical cations, eq 1 can be approximated by

$$g - g_{\mathrm{e}} \propto \lambda \tag{2}$$

The spin−orbit coupling constants for sulfur and selenium are $\lambda_{\mathrm{S}} = 382$ and $\lambda_{\mathrm{Se}} = 1688\ \mathrm{cm}^{-1}$, respectively;[34] the deviations of their g factors from the free-spin value should reflect the magnitude of their spin−orbit coupling constants. Indeed, the ratio by which the g factors of **2b**$^{\bullet+}$ and **1a**$^{\bullet+}$,**b**$^{\bullet+}$ deviate from the free-spin value, $(g_{\mathrm{S}} - g_{\mathrm{e}})/(g_{\mathrm{Se}} - g_{\mathrm{e}}) = 0.195$, is in reasonable agreement with the ratio of the spin−orbit coupling constants, $\lambda_{\mathrm{S}}/\lambda_{\mathrm{Se}} = 0.226$.

We also investigated the DR spectra of the newly prepared radical cations, **1a**$^{\bullet+}$, **b**$^{\bullet+}$. The open-shell configurations of organic radical cations introduce electronic transitions of much lower energies without precedent in the neutral precursors. They appear as characteristic transitions in the visible or even the near-IR (NIR). Indeed, significantly shifted absorption maxima are considered unambiguous evidence for the formation of radical cations. The DR UV−vis spectrum of the diselena radical

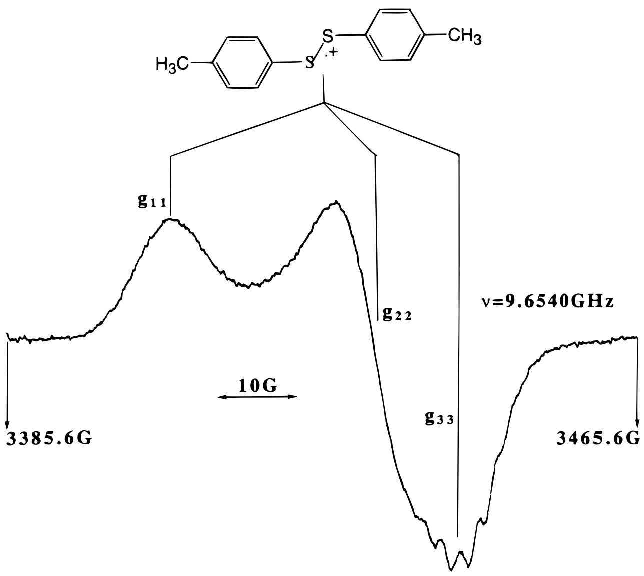


Figure 2. X-band EPR spectrum obtained upon sequestering bis-*p*-tolyl disulfide (**2b**) in Na-ZSM-5. The principal g values, $g_1 = 2.0247$, $g_2 = 2.0095$, and $g_3 = 2.0034$, assigned to the radical cation, **2b**$^{\bullet+}$, are indicated in the spectrum.

cation, **1a**$^{\bullet+}$, incorporated within pentasil zeolite, exhibits a pair of bands at $\lambda_{\max} = 520$ and 550 nm of medium intensity and a broad absorption feature at $\lambda_{\max} \sim 950$ nm (Figure 3). Since the parent molecule, **1a**, does not absorb beyond 300 nm, this spectrum is considered strong evidence for the formation of **1a**$^{\bullet+}$ in the zeolite.

The DR spectra of **1a**$^{\bullet+}$ and **2a**$^{\bullet+}$ may eventually offer the opportunity to compare the three-electron π-bonds of diselenides and disulfides. The optical bands corresponding to the electronic transitions of lowest energy have been assigned to $\pi-\pi^*$ transitions associated with the three-electron π-bond of these radical cations. It is tempting to interpret the different transition energies of the broad bands near 950 (**1a**$^{\bullet+}$) and 800 nm (**2a**$^{\bullet+}$; Figure 2) in terms of different π-bond energies; this assignment is in line with the bond strengths assigned to other pairs of congeners. However, a comparison with the (most thoroughly investigated) optical spectra of hydrazine radical cations with two-center three-electron π-bonds[35] indicates that this assignment will have to await further study.

The optical spectra of a wide range of hydrazine radical cations show significant variations in $\pi-\pi^*$ transition energies (absorption maxima, 265 nm $< \lambda_{\max} <$ 455 nm).[35] These species have the two-center three-electron bond in common, but differ in various other aspects, for example, the extent of steric crowding or the hybridization of the heteroatoms. However, their π-bond energies may not vary significantly. Concerning the disulfide and diselenide radical cations, their (enforced) extended conformation, the significantly longer bonds (e.g., S$-$S, 2.07 Å;[12] N$-$N, 1.35 Å), and the "simple" aryl substituents tend to diminish the role of steric factors. Other factors cannot be evaluated, given that only two basically similar examples are being reported. Thus, it remains unclear whether a direct relationship exists between the $\pi-\pi^*$ transition energies of the disulfide and diselenide radical cations and the strengths of their two-center three-electron π-bonds.

In conclusion, incorporation into pentasil zeolite converts **1a**, **b**, and **2b** to "extended" radical cations, **1a**$^{\bullet+}$, **b**$^{\bullet+}$, and **2b**$^{\bullet+}$, which have not been observed previously. Their formation occurs by oxidation at a redox-active site in the zeolite; their persistence is ascribed to favorable factors, such as exclusion of potential reagents and stabilization of the extended conformer by the narrow ZSM-5 channels, which prevent the conformational rearrangement required for oxidative cyclization to **3a**$^{\bullet+}$ (X = Se).

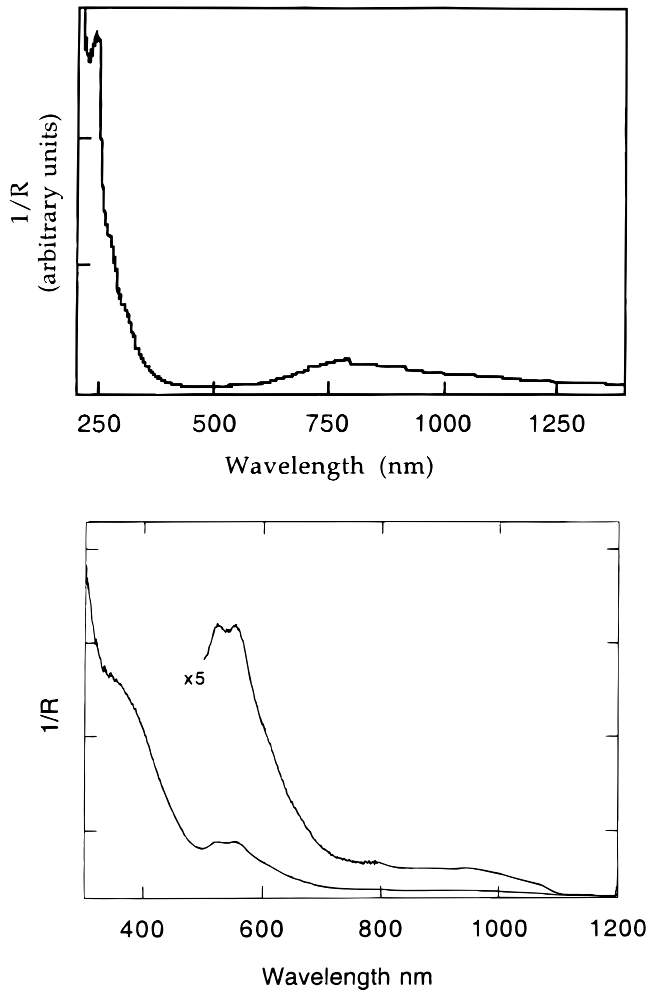


Figure 3. Diffuse reflectance spectra (plotted as the inverse of the reflectance, 1/*R*) of H-ZSM-5 zeolite after incorporation of diphenyl diselenide, **1a** (bottom), and diphenyl disulfide, **2a** (top).

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References and Notes

(1) *Zeolite Microporous Solids: Synthesis, Structure, and Reactivity*; Derouane, E. G., Lemos, F., Naccache, C., Rebeiro, F. R., Eds.; Kluwer Academic Publishers: Norwell, MA, 1991.

(2) Izumi, Y.; Urabe, K.; Onaka, M. *Zeolite, Clay, and Heteropoly Acid in Organic Reactions*; Verlag Chemie: Weinheim, 1992.

(3) *Radicals on Surfaces*; Lund, A., Rhodes, C. J., Eds.; Kluwer Academic Publishers: Dordrecht, 1995.

(4) Ramamurthy, V.; Casper, C. V.; Corbin, D. R. *J. Am. Chem. Soc.* **1991**, *113*, 594−600.

(5) Chen, F. R.; Fripiat, J. J. *J. Phys. Chem.* **1992**, *96*, 819−823, **1993**, *97*, 5796−5797.

(6) Rhodes, C. J.; Reid, I. D.; Roduner, E. *J. Chem. Soc., Chem. Commun.* **1993**, 512−513.

(7) Corma, A.; Fornes, V.; Garcia, H.; Marti, V.; Miranda, M. A. *Chem. Mater.* **1995**, *7*, 2136.

(8) Toriyama, K.; Nunome, K.; Iwasaki, M. *J. Am. Chem. Soc.* **1987**, *109*, 4496−4500.

(9) Lakkaraju, P. S.; Zhang, J.; Roth, H. D. *J. Phys. Chem.* **1994**, *98*, 2722.

(10) Lakkaraju, P. S.; Zhou, D.; Roth, H. D. *Chem. Commun.* **1996**, 2605−2606.

(11) Lakkaraju, P. S.; Zhou, D.; Roth, H. D. *J. Chem. Soc., Perkin Trans. 2* **1998**, 1119−1121.

(12) Martí, V.; Fernández, L.; Fornés, V.; García, H.; Roth, H. D. *J. Chem. Soc., Perkin Trans. 2* **1999**, 145−152.

(13) Yokoi, H.; Hatta, A.; Ishiguro, K.; Sawaki, Y. *J. Am. Chem. Soc.* **1998**, *120*, 12728−12733.

(14) Asmus, K. D. *Acc. Chem. Res.* **1979**, *12* (12), 436−442.

(15) Illies, A. J.; Livant, P.; McKee, M. L. *J. Am. Chem. Soc.* **1988**, *110*, 7980−7984.

(16) Clark, T. *J. Am. Chem. Soc.* **1988**, *110*, 1672−1678.

(17) Qin, X.-Z.; Meng, Q.-C.; Williams, F. *J. Am. Chem. Soc.* **1987**, *109*, 6778−6788.

(18) Musker, W. K. *Acc. Chem. Res.* **1980**, *13*, 200−206.

(19) Morihashi, K.; Kushihara, S.; Inadomi, Y.; Kikuchi, O. *J. Mol. Struct. (THEOCHEM)* **1997**, *418*, 171−178.

(20) Bock, H.; Stein, U. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 834−835.

(21) Bock, H.; Stein, U.; Semkow, A. *Chem. Ber.* **1980**, *113*, 3208−3220.

(22) Russel, G. A.; Zaleta, M. *J. Am. Chem. Soc.* **1982**, *104*, 2318.

(23) Russel, G. A.; Law, W. C.; Zaleta, M. *J. Am. Chem. Soc.* **1985**, *107*, 4175.

(24) EPR samples were prepared by stirring 2−3 mg of the substrate with 70 mg of zeolite (Na-ZSM5, thermally activated by calcination at 500 °C for 12 h, and stored under argon) in 10 mL of 2,2,4-trimethylpentane for 2 h. The loaded zeolite is collected by filtration, washed with hexane, and dried under vacuum (0.001 Torr).

(25) Although formally neutral, the zeolite sample contained both Lewis and Brønsted acid sites according to the pyridine adsorption/desorption method.[12]

(26) Wendlandt, W. W.; Hecht, H. G. *Reflectance Spectroscopy*; Wiley: New York, 1966.

(27) Chiu, M. F.; Gilbert, B. C. *J. Chem. Soc., Perkin Trans. 2* **1973**, 258.

(28) Lamotte, B.; Berthier, G. *J. Chim. Phys.* **1966**, *63*, 369.

(29) Giordan, J.; Bock, H. *Chem. Ber.* **1982**, *115*, 2548.

(30) Roth, H. D.; Shen, K.; Lakkaraju, P. S.; Fernández, L. *Chem. Commun.* **1998**, 2447−2448.

(31) Stone, A. J. *Mol. Phys.* **1963**, *6*, 509.

(32) Segal, B. G.; Kaplan, M.; Fraekel, G. K. *J. Chem. Phys.* **1965**, *43*, 4191.

(33) Biehl, R.; Plato, M.; Moebius, K. *Mol. Phys.* **1978**, *35*, 985.

(34) Hirayama, M.; Terasaka, T.; Itasaka, M.; Suzuki, T.; Yamashita, Y.; Miyashi, T. *Chem. Lett.* **1995**, 837−838.

(35) Nelsen, S. F.; Tran, H. Q.; Ismagilor, R. F.; Ramm, M. T.; Chen, L.-J.; Powell, D. R. *J. Org. Chem.* **1998**, *63*, 2536−2543, and references therein.