

pressions for the magnetic tensors by taking into account mixing with all states resulting from singly excited configurations²⁵ does not alter the above results significantly.

Our results indicate that free $\text{Mn}(\text{cp})_2$ and $\text{Mn}(\text{mecp})_2$ molecules are so close to the low-spin-high-spin crossover point that the small intermolecular forces as present in frozen solutions or molecular crystals are sufficient for inducing the observed changes in the electronic ground state configuration. Consistent with ligand field theoretical expectations the high-spin ground state is found preferentially in host systems favoring large metal to ring distances, while the low-spin ground state is induced by sandwich matrices exhibiting short metal to ring distances.

We conclude that the most reasonable explanation of the anomalous magnetic behavior²⁻⁷ of undiluted $\text{Mn}(\text{cp})_2$ and $\text{Mn}(\text{mecp})_2$ is a temperature dependent high-spin-low-spin equilibrium. We found that a large part of the $\chi_m(T)$ curve^{3,4} of $\text{Mn}(\text{cp})_2$ below the transition point can even be explained by an almost constant energy difference $E(^6A_{1g}) - E(^2E_{2g}) \approx +0.5$ kcal/mol. This interpretation is consistent with our observation that the broad esr signal⁷ of pure $\text{Mn}(\text{cp})_2$ at $g = 2$ disappears completely at 4.2°K; this band must be due to the thermally populated high-spin state.

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References and Notes

- (1) F. Engelmann, *Z. Naturforsch. B*, **8**, 775 (1953).
- (2) (a) E. O. Fischer and H. Leipfinger, *Z. Naturforsch. B*, **10**, 353 (1955); (b) H. Leipfinger, *ibid.*, **13**, 53 (1958).
- (3) G. Wilkinson, F. A. Cotton, and J. M. Birmingham, *J. Inorg. Nucl. Chem.*, **2**, 95 (1956).
- (4) L. T. Reynolds and G. Wilkinson, *J. Inorg. Nucl. Chem.*, **9**, 86 (1959).
- (5) G. Wilkinson and F. A. Cotton, *Progr. Inorg. Chem.*, **1**, 1 (1959).
- (6) E. O. Fischer and H. P. Fritz, *Advan. Inorg. Chem. Radiochem.*, **1**, 55, (1959).
- (7) J. Voittländer and E. Schimitschek, *Z. Elektrochem.*, **61**, 941 (1957).
- (8) K. D. Warren, *Inorg. Chem.*, **13**, 1243 (1974).
- (9) K. D. Warren, *Inorg. Chem.*, **13**, 1317 (1974).
- (10) R. Krieger and J. Voittländer, *Z. Naturforsch. A*, **27**, 1082 (1972).
- (11) J. W. Rabalais, L. O. Werme, T. Bergmark, L. Karlsson, M. Hussain, and K. Siegbahn, *J. Chem. Phys.*, **57**, 1185 (1972).
- (12) S. Evans, M. L. H. Green, B. Jewitt, G. H. King, and A. F. Orchard, *J. Chem. Soc., Faraday Trans. 2*, 356 (1974).
- (13) R. D. Dowsing and J. F. Gibson, *J. Chem. Phys.*, **50**, 294 (1968).
- (14) R. D. Dowsing, J. F. Gibson, M. Goodgame, and P. J. Hayward, *J. Chem. Soc. A*, 187 (1969).
- (15) W. V. Sweeney, D. Coucouvanis, and R. E. Coffman, *J. Chem. Phys.*, **59**, 369 (1973).
- (16) R. Prins, *Mol. Phys.*, **19**, 603 (1970).
- (17) A. H. Maki and T. E. Berry, *J. Amer. Chem. Soc.*, **87**, 4437 (1965).
- (18) D. N. Hendrickson, Y. S. Sohn, and H. B. Gray, *Inorg. Chem.*, **10**, 1559 (1971).
- (19) S. E. Anderson and R. Rai, *Chem. Phys.*, **2**, 216 (1973).
- (20) J. H. Ammeter and J. D. Swalen, *J. Chem. Phys.*, **57**, 678 (1972).
- (21) J. H. Ammeter and J. M. Brom, *Chem. Phys. Lett.*, **27**, 380 (1974).
- (22) E. R. Lippincott and R. D. Nelson, *Spectrochim. Acta*, **10**, 307 (1957).
- (23) J. J. Fortman and R. G. Hayes, *J. Chem. Phys.*, **43**, 15 (1965).
- (24) M-M. Coutière, J. Demuyneck, and A. Veillard, *Theor. Chim. Acta*, **27**, 281 (1972).
- (25) J. H. Ammeter, 1974, unpublished.

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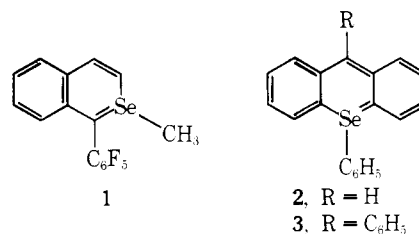
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Synthesis and Characterization of a Selenabenzene¹

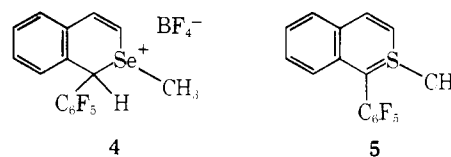
Sir:

Thiabenzene recently have been the subject of thorough investigations.²⁻⁴ We now report the first example of an authentic selenabenzene, 1-pentafluorophenyl-2-methyl-2-

selenanaphthalene (**1**), and present evidence which refutes earlier claims^{5,6} for stable 10-selenaanthracenes **2** and **3**.



Reaction of 2-selenanaphthalenium perchlorate⁷ with pentafluorophenylmagnesium bromide in ether furnished 1-pentafluorophenyl-2-seleno-3-chromene (60%) which upon methylation with silver tetrafluoroborate-methyl iodide gave 1-pentafluorophenyl-2-methyl-2-seleno-3-chromenium tetrafluoroborate (**4**), (78%) as a mixture of diastereomers (1/2.8 cis/trans, by nmr).¹⁰ Treatment of the diastereomeric mixture with dimsyl-*d*₅-lithium (1 equiv) in toluene-*d*₈-1,2-dimethoxyethane under nitrogen at low temperature¹¹ immediately produced a deep burgundy solution. The ¹H nmr spectrum¹² indicated that this solution contained **1**. Notable features were the characteristic up-field doublet of the 3-vinyl proton and the side bands accompanying the methyl singlet due to ⁷⁷Se-¹H scalar coupling. The ⁷⁷Se-¹H side bands clearly attest to the presence of a selenium-methyl bond,¹³ and the high field doublet¹² at δ 4.89 reflects the ylide nature of the selenabenzene,¹⁴ a phenomenon seen with the corresponding thiabenzene, 1-pentafluorophenyl-2-methyl-2-thianaphthalene (**5**), for



which δ 4.76 (d, ³J_{HH} = 8 Hz) was observed.^{3,17} In the presence of DMSO-*d*₆, further splitting of the methyl and 4-vinyl proton signals was observed. This is reasonably attributed to deuterium coupling, the deuterium being incorporated by an exchange reaction with the solvent at the methyl and 3-vinyl positions.¹⁸

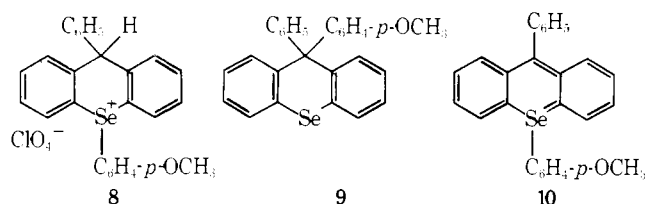
The absorption band responsible for the intense color of **1** has λ_{max} 500 nm (DMSO), closely comparable to the λ_{max} 480 nm (DMSO) observed for **5** and to the λ_{max} in the visible region of other authentic thiabenzene.³ The structure for **1** is also supported by mass spectral data.¹⁹

When the burgundy solution was allowed to stand at room temperature, thermal decomposition rapidly took place, as evinced by decolorization of the sample to a pale orange. Decay of the original sample was confirmed by ¹H nmr.²⁰ The visible spectrum of **1** was monitored with time to afford the interval for 50% decomposition (first half-life) of 47 min at 25°.²¹

It is apparent that **1** has a lifetime between two and three orders of magnitude shorter than the sulfur analog **5** under the same conditions, 249 hr.³ This order of relative stabilities may be presumed to exist between other structurally analogous seleno- and thiabenzene. The instability of **1** points to the fact that selenabenzene, unless substituted by strongly electron withdrawing groups, are not likely to exhibit sufficient stability to be readily observed.

In light of these conclusions, the reported^{5,6} synthesis and isolation of **2** and **3** and their description as stable compounds appeared suspect, particularly so since the physical properties of these solids were strikingly reminiscent of those^{22,23} displayed by materials previously characterized

as "stable thiabenzenes," which have been shown not to be authentic thiabenzenes.² Indeed, treatment of 10-selenoxanthylum and 9-phenyl-10-selenoxanthylum perchlorates with excess phenyllithium in ether, as described,⁵ afforded powdery tan solids **6** and **7**, respectively.²⁴ Both of these products are evidentially (molecular weights; mass, nmr, and uv spectra) not 10-selenaanthracenes **2** and **3** but are oligmers of undetermined composition. This conclusion is consistent with the observation^{5,6} that deprotonation of 9-phenyl-10-*p*-anisylselenoxanthylum perchlorate (**8**) by sodium hydride in tetrahydrofuran is followed by rearrangement to 9-phenyl-9-*p*-anisylselenoxanthene (**9**). Since this reaction must proceed through a 10-selenaanthracene intermediate, **10**, the latter can only have a transient existence,



in complete analogy with the corresponding sulfur compounds.² Thus, the solid substances isolated⁵ from the reaction of phenyllithium with selenoxanthylum salts are assuredly not selenaanthracenes.

References and Notes

- (1) This work was supported by the National Science Foundation (GP-30257).
- (2) G. H. Senkler, Jr., J. Stackhouse, B. E. Maryanoff, and K. Mislow, *J. Amer. Chem. Soc.*, **96**, 5648 (1974).
- (3) J. Stackhouse, B. E. Maryanoff, G. H. Senkler, Jr., and K. Mislow, *J. Amer. Chem. Soc.*, **96**, 5650 (1974).
- (4) B. E. Maryanoff, G. H. Senkler, Jr., J. Stackhouse, and K. Mislow, *J. Amer. Chem. Soc.*, **96**, 5651 (1974).
- (5) M. Hori, T. Kataoka, H. Shimizu, and C.-F. Hsü, *Chem. Lett.*, 391 (1973).
- (6) M. Hori, T. Kataoka, H. Shimizu, C.-F. Hsü, Y. Asahi, and E. Mizuta, *Chem. Pharm. Bull.*, **22**, 32 (1974).
- (7) This compound was prepared by a modification of the procedure of Renson and Pirson.⁸ α, α' -Diseleno-*o*-toluic acid⁹ was converted to 4-acetoxy-2-seleno-3-chromene, and the product was simultaneously hydrolyzed and reduced to 2-selenochroman-4-ol with sodium borohydride in aqueous ethanolic sodium hydroxide (83%). The alcohol was then converted to 2-selenanaphthalenium perchlorate by the reported procedure.⁸
- (8) M. Renson and P. Pirson, *Bull. Soc. Chim. Belg.*, **75**, 456 (1966).
- (9) W. H. H. Günther, *J. Org. Chem.*, **32**, 3929 (1967).
- (10) The pure trans isomer (¹H nmr $\delta^{\text{TMS}}(\text{CD}_3\text{CN})$ 2.91 (s, 3 H, ⁷⁷Se side bands at ± 5 Hz), 6.52 (s, 1 H), 6.77 (d, 1 H, ³J_{HH} = 9 Hz), 7.20–7.75 (m, 5 H)), mp 160.5–161° dec (sealed capillary), and a 2/3 mixture of cis/trans isomers (¹H nmr $\delta^{\text{TMS}}(\text{CD}_3\text{CN})$ 2.63 (t, 3 H, ⁸J_{HF} (?) = 2 Hz), 6.68 (s, 1 H), 6.91 (d, 1 H, ³J_{HH} = 9 Hz), 7.15–7.75 (m, 5 H) plus the signals for the trans isomer in the appropriate ratio of peak heights), mp 156–157° dec (sealed capillary), were isolated by fractional crystallization. Both gave satisfactory elemental analyses. Assignment of the isomers was tentatively made by ¹H nmr; the cis isomer was associated with the triplet methyl signal, the multiplicity presumably arising from long-range through space coupling to the ortho fluorine nuclei on the (cis) pentafluorophenyl ring.
- (11) This procedure was the same as that used for the preparation of unstable thiabenzenes.³
- (12) ¹H nmr (toluene-*d*₈–1,2-dimethoxyethane 0.40 ml/30 μ l) δ^{TMS} 1.20 (s, 3 H, ⁷⁷Se side bands at ± 6 Hz), 4.89 (d, 1 H, ³J_{HH} = 8 Hz), 6.50–7.25 (m, 6.1 H). Embedded in the multiplet is a signal at δ 6.73 (d, ³J_{HH} = 8 Hz).
- (13) U. Svanholm, "Organic Selenium Compounds: Their Chemistry and Biology," D. L. Klayman and W. H. H. Günther, Ed., Wiley, New York, N.Y., 1973, pp 903–932.
- (14) Highly stabilized selenonium ylides have recently been prepared,¹⁵ and selenonium ylides have also recently been used in organic synthesis.¹⁶
- (15) K.-T. H. Wei, I. C. Paul, M.-M.Y. Chang, and J. I. Musher, *J. Amer. Chem. Soc.*, **96**, 4099 (1974), and references cited therein; N. N. Magdesieva, R. A. Kandgetcyan, and A. A. Ibragimov, *J. Organometal. Chem.*, **42**, 399 (1972).
- (16) W. Dumont, P. Bayet, and A. Krief, *Angew. Chem., Int. Ed. Engl.*, **13**, 274 (1974).
- (17) See also A. G. Hortmann and R. L. Harris, *J. Amer. Chem. Soc.*, **92**, 1803 (1970).
- (18) Deuterium exchange has been reported in the generation of thiabenzenes by deprotonation in DMSO-*d*₆.¹⁷
- (19) Mass spectrum (70 eV, material generated *in situ* by heating **4** pulverized with sodium hydroxide on the sample probe at 80°) *m/e* (rel abundance, %) 376 (18), 374 (9), 363 (11), 362 (43), 361 (28), 360 (23), 359 (21), 358 (13), 341 (10), 296 (11), 295 (48), 294 (10), 282 (26), 281 (100), 275 (12), 274 (15), 261 (23), 255 (10), 195 (13), 193 (13), 121 (23), 115 (26) (peaks reported $\pm 10\%$ relative abundance). Exact mass: calcd, 375.9789; found, 375.980 \pm 0.004. A similar spectrum was obtained from material from an nmr sample of **1**.

- (20) 1-Pentafluorophenyl-2-seleno-3-chromene was isolated (ca. 30%) from the decomposition mixture by chromatography on florisisil with hexane eluent.
- (21) The procedure was the same as the one used to monitor the thermal decomposition of thiabenzenes by their visible spectrum.³
- (22) C. C. Price, M. Hori, T. Parasaran, and M. Polk, *J. Amer. Chem. Soc.*, **85**, 2278 (1963).
- (23) M. Polk, M. Siskin, and C. C. Price, *J. Amer. Chem. Soc.*, **91**, 1206 (1969).
- (24) For **6**: mp 135–155°. *Anal.* Calcd for C₁₉H₁₄Se: C, 71.03; H, 4.39. Found: C, 67.88; H, 4.43. Molecular weight: calcd, 321; found, 973 (osmometry in benzene). The ¹H nmr spectrum of this material featured a broad envelope absorption centered at $\delta^{\text{TMS}}(\text{CDCl}_3)$ 7.2 ($W_{1/2} = 0.5$ ppm) and additional minor signals at 5.28 and 1.5–0.5 (aliphatic region). The uv spectrum (ethanol) of this material showed a broad absorption, tailing into the visible (220–450 nm) with shoulders (λ_{max} (log ϵ)) at 275 (3.83) and 255 (3.94) nm. The reported maximum⁵ at 211 nm is due to uv cutoff of the solvent. The mass spectrum (70 eV) of this material showed peaks at *m/e* (rel abundance, %) 338 (10), 336 (6), 324 (5), 323 (8), 322 (26), 321 (15), 320 (15), 319 (13), 318 (8), 317 (5), 261 (22), 246 (85), 244 (46), 242 (20), 165 (52), 164 (69), 154 (100), 153 (26), 152 (40), 149 (29), 94 (25), 77 (28), 76 (23), 71 (74), 70 (33), 69 (21), in addition to minor peaks from *m/e* 400–700. Only peaks with a relative abundance greater than 20% are reported below *m/e* 300. For **7**, two fractions, **7a** and **7b**, were obtained by repeated work-up of the crude reaction mixture. **7a** (less soluble fraction) mp 140–160°. *Anal.* Calcd for C₂₅H₁₈Se: C, 75.56; H, 4.57. Found: C, 74.83; H, 4.98. Molecular weight: calcd, 397; found, 986 (osmometry in benzene). The ¹H nmr spectrum of this material featured a broad absorption envelope centered at $\delta^{\text{TMS}}(\text{CDCl}_3)$ 7.2 ($W_{1/2} = 0.5$ ppm) and additional minor absorptions in the aliphatic region (1.5–0.5). The uv spectrum (ethanol) of this material showed a broad absorption, tailing into the visible (220–550 nm) with shoulders (λ_{max} (log ϵ)) at 280 (4.23) and 260 (4.31) nm. The reported maximum⁵ at 211 nm is due to uv cutoff of the solvent. The mass spectrum (70 eV) of this material showed peaks at *m/e* (rel abundance, %) 476 (1), 475 (2), 474 (5), 473 (2), 472 (3), 471 (2), 470 (2), 455 (2), 409 (2), 400 (6), 399 (15), 398 (31), 397 (47), 396 (18), 395 (33), 394 (15), 393 (13), 392 (2), 391 (2), 323 (38), 322 (55), 321 (100), 320 (36), 319 (99), 318 (41), 317 (46), 245 (63), 243 (31), 241 (38), 240 (20), 239 (57), 165 (28), in addition to minor peaks beyond *m/e* 500. Only peaks with a relative abundance greater than 20% are reported below *m/e* 390. **7b** (more soluble fraction) mp 95–120°. *Anal.* Calcd for C₂₅H₁₈Se: C, 75.56; H, 4.57. Found: C, 75.25; H, 4.99. Molecular weight: Calcd, 397; Found, 737 (osmometry in benzene). The ¹H nmr spectrum (CDCl₃) and uv spectrum (ethanol) were closely similar to those of **7a**. The mass spectrum (70 eV) showed peaks at *m/e* (rel abundance, %) 476 (1), 475 (1), 474 (3), 473 (1), 472 (2), 471 (1), 455 (2), 453 (1), 401 (2), 400 (8), 399 (17), 398 (40), 397 (49), 396 (23), 395 (33), 394 (16), 393 (12), 392 (2), 391 (2), 323 (35), 322 (46), 321 (100), 320 (28), 319 (99), 318 (37), 317 (43), 245 (27), 241 (26), 239 (42), in addition to minor peaks beyond *m/e* 500. Only peaks with a relative abundance greater than 20% are reported below *m/e* 390.

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¹⁸O Exchange Studies on V₁₀O₂₈⁶⁻ in Aqueous Media

Sir:

Over recent years a continuing interest has been shown in the aqueous polymerization of ions of the type MO₄ⁿ⁻, including VO₄³⁻.^{1,2} While the understanding of the vanadium system has improved, little structural information nor modes of reaction are available even in aqueous media. The decavanadate ion V₁₀O₂₈⁶⁻ appears to be a well-defined, easily prepared ion³ and may be the best starting point for future studies in the vanadium(V) system. Thus it is vital that the aqueous nature of this ion be well understood. While solid structures containing the ion have been reported^{4,5} they can only suggest the structure of the ion in solution. Likewise the precise potentiometric and spectral studies^{6,7} do not give much information about the exact species present in solution. A kinetic study of oxygen exchange between solutions of (NH₄)₆V₁₀O₂₈·6H₂O and H₂O