complete or incomplete before reopening to *sec*-butyl ion, but the maximum effect on the rate constants resulting from this difference is a factor of $^3/_2$, and therefore only an insignificant change in the log A term would result. Assuming complete mixing and fitting the rates to the Arrhenius equation yielded $E_a = 7.5 \pm 0.1$ kcal/mol and log $A = 12.3 \pm 0.1$, where errors reported are standard deviations.

Attempted formation of a secondary amyl cation from either 2-chloropentane or 1-chloropentane under the same conditions has so far led only to *t*-amyl cation. Cyclization of the initial secondary ion to protonated dimethylcyclopropane here could, after proton shifts, lead to a species which could open to the 3-methyl-2-butyl cation, an isomeric secondary ion only a single hydride shift away from the *t*-amyl cation.[8] The methylcyclopropane intermediate can lead to the *t*-butyl cation by a similar opening, only by first forming the high-energy primary isobutyl cation.

Acknowledgment. We thank the National Science Foundation for support of this work.

[8] M. Saunders and E. L. Hagen, *J. Am. Chem. Soc.*, **90**, 2436 (1968).

[9] Fellow of the Alfred P. Sloan Foundation.

[10] National Institutes of Health Predoctoral Fellow.

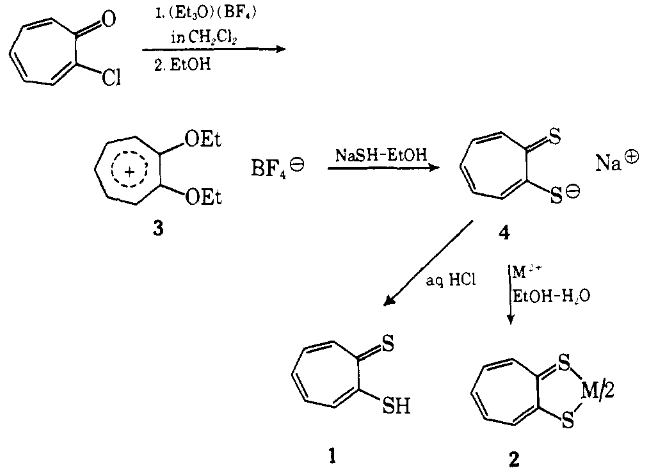
Martin Saunders,[9] Edward L. Hagen,[10] Jerold Rosenfeld[10]
Yale University
New Haven, Connecticut 06520
Received September 3, 1968

Dithiotropolone (2-Mercaptocycloheptatrienethione) and Its Metal Complexes

Sir:

The preparation of tropolone in 1950[1] has been followed by the synthesis of a variety of monoprotic, chelating, 1,7-disubstituted 1,3,5-cycloheptatrienes, *viz.*, the aminotropones,[2] aminotroponeimines,[2b,3] aminothiotropones,[3b,4,5] and 2-mercaptotropone.[6] These compounds, of much interest in their own right, form stable metal complexes[2b,7] whose structural and electronic properties are of considerable current significance.[7] This information, together with continuing research on sulfur-bonded chelates with nonclassical electronic ground states,[8] renders dithiotropolone (**1**) and its complexes attractive synthetic objectives. We report here the synthesis of hitherto unknown **1** and a series of its bis complexes **2**.

2-Chlorotropone,[2a] obtained from tropolone,[9] was treated with 1 equiv of triethyloxonium tetrafluoroborate in dichloromethane solution for 20 hr at ~25°. Removal of solvent followed by refluxing of the resultant solid in absolute ethanol for 2 hr and recrystallization of the product from THF yielded 1,2-diethoxytropylium tetrafluoroborate[10] (**3**) (65%): mp 115–116°, nmr ($CDCl_3$) τ 8.18 (triplet, 6, CH_3), 5.17 (quartet, 4, CH_2), 1.33 (multiplet, 5, ring-H). Treatment of **3** with 2 equiv of sodium hydrosulfide in ethanol followed by 15 min of stirring at ~25° and removal of solvent afforded sodium dithiotropolonate (**4**) as a reddish brown solid which was not further purified. Anaerobic reaction of **4** with dilute aqueous hydrochloric acid and slow sublimation (35°, 10^{-4} mm) of the impure product gave deep red-brown, crystalline **1**[11] in low yield: mp 72–73°; nmr ($CDCl_3$) τ 2.95 (multiplet, 3, ring-H), 1.57 (multiplet, 2, ring-H), 0.76 (1, SH); mass spectrum (70 eV) *m/e* (relative intensity) 154 (100, P), 153 (86), 121 (55), 110 (35), 90 (32), 89 (31), 77 (52). Dithiotropolone is less stable than tropolone and should be handled in the absence of air.



Dithiotropolonate metal complexes, $M(SST)_2$, are readily prepared from aqueous ethanol solutions of **4** and the appropriate metal salt. As a class the complexes are stable to air and moisture, intensely colored, very slightly soluble in noncoordinating solvents, and somewhat more soluble in pyridine and DMF. Complexes of Ni (black), Pd (violet), Pt (black), Cu (greenish black), Zn (red), and Cd (red-brown) have been obtained in 25–50% yield based on **3**. All are diamagnetic except for $Cu(SST)_2$ whose isotropic epr parameters ($\langle g \rangle = 2.041$, $\langle a \rangle = 78$ G (^{63}Cu), CH_2Cl_2 solution) are entirely typical of spin-doublet [$Cu-S_4$] complexes.[8b] The mass spectra of the Ni and Zn complexes evidence prominent parent ion peaks and rather similar fragmentation patterns leading to $MC_7H_5S_2^+$ and, like **1**, $C_7H_5S_2^+$, $C_7H_5S^+$, $C_7H_5^+$, and $C_6H_5^+$ among the major products.

That these complexes do possess the dithiotropolonate structure **2** rather than that of the analytically indistinguishable rearrangement products **5** has been demonstrated by comparison of certain properties with those of bisdithiobenzoate complexes, $M(dtb)_2$, which

---

[1] For a recent summary of tropolone chemistry, *cf.* D. Lloyd, "Carbocyclic Non-Benzenoid Aromatic Compounds," Elsevier Publishing Co., Amsterdam, 1966, Chapter VI.

[2] (a) W. von E. Doering and L. H. Knox, *J. Am. Chem. Soc.*, **74**, 5683 (1952); (b) W. R. Brasen, H. E. Holmquist, and R. E. Benson, *ibid.*, **83**, 3125 (1961); (c) N. Soma, J. Nakazawa, T. Watanabe, Y. Sato, and G. Sunagawa, *Chem. Pharm. Bull.* (Tokyo), **13**, 457 (1965).

[3] (a) H. Nakao, *ibid.*, **13**, 810 (1965); (b) N. Soma, J. Nakazawa, T. Watanabe, Y. Sato, and G. Sunagawa, *ibid.*, **13**, 819 (1965).

[4] W. R. Brasen and R. E. Benson, *J. Am. Chem. Soc.*, **83**, 3135 (1961).

[5] T. Nozoe and K. Matsui, *Bull. Chem. Soc. Japan*, **34**, 1382 (1961).

[6] T. Nozoe, M. Sato, and K. Matsui, *Proc. Japan Acad. Sci.*, **29**, 22 (1953); *Sci. Rept. Tohoku Univ., First Ser.*, **37**, 211 (1953).

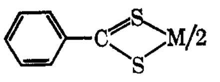
[7] (a) E. L. Muetterties, H. Roesky, and C. M. Wright, *J. Am. Chem. Soc.*, **88**, 4856 (1966); (b) W. R. McClellan and R. E. Benson, *ibid.*, **88**, 5165 (1966); (c) D. R. Eaton, W. D. Phillips, and D. J. Caldwell, *ibid.*, **85**, 397 (1963).

[8] (a) R. H. Holm, A. L. Balch, A. Davison, A. H. Maki, and T. E. Berry, *ibid.*, **89**, 2866 (1967), and references therein; (b) J. A. McCleverty, *Progr. Inorg. Chem.*, in press.

[9] H. C. Stevens, D. A. Reich, D. R. Brandt, K. R. Fountain, and E. J. Gaughan, *J. Am. Chem. Soc.*, **87**, 5257 (1965).

[10] All new compounds gave satisfactory elemental analyses except for **4**, whose purity was not assessed.

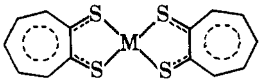
[11] *Anal.* Calcd for $C_7H_6S_2$: C, 54.51; H, 3.92; S, 41.57. Found: C, 54.51; H, 3.92; S, 41.56.



5

have recently been characterized in detail.[12] Taking $Ni(SST)_2$ and $Ni(dtb)_2$ as examples, their infrared spectra (mull, 1500–400 cm^{-1}) and electronic and mass spectra are markedly different. In particular, $Ni(dtb)_2$ shows only a weak parent ion peak and a fragmentation pattern clearly dissimilar to that of $Ni(SST)_2$. No d–d absorption band such as that at 13,200 cm^{-1} ($\epsilon \sim 980$) observed in the spectrum of $Ni(dtb)_2$[12c] can be found in the spectrum of $Ni(SST)_2$, which in the 11,000–15,000-cm^{-1} range consists of two intense features at 13,500 cm^{-1} (ϵ 14,600) and 15,200 cm^{-1} (sh, $\epsilon \sim 7300$). Further prominent spectral differences between the Ni, Pd, and Pt complexes of the SST and dtb series[12c] are observed in the 15,000–35,000-cm^{-1} region.

The electronic ground-state description of the bisdithiotropolonates represents an interesting problem. Adopting a qualitative valence-bond approach,[8a,13] structures such as **2** in which the metal has the *formal* oxidation state II lead to the delocalized formulation **6**



6

for $M(SST)_2$. A probable consequence of the delocalized electronic structure is the observed polarographic reducibility of these complexes. For example, $Ni(SST)_2$ and $Pd(SST)_2$ show one-electron reductions with $E_{1/2}$ -0.69 and -0.67 V,[14] respectively. A second, less well-defined wave is observed at -1.06 (Ni) and -0.98 V (Pd). $Zn(SST)_2$ and $Cd(SST)_2$ exhibit two apparently single-electron reductions at -0.66, -0.88 (Zn) and -0.69, -0.89 V (Cd). This behavior is similar to that now well recognized for other series of complexes containing delocalized five-membered chelate rings, *viz.*, the Ni, Pd, and Pt neutral dithiolenes, $[MS_4C_4R_4]^0$, and 1,2-disubstituted benzenes and derivatives, $[M(C_6H_4XY)_2]^0$ (X, Y = NH, O, S),[8b,13,15] and the Ni, Zn, and Cd complexes $[M(gma)]^0$ and $[M(dtbh)]^0$.[8a] However, the electronic structural features responsible for this behavior may not be the same as those of, *e.g.*, the bisdithiolenes. A *strictly analogous* set of contributing VB structures, which furnish a satisfactory, simple ground-state description of $[MS_4C_4R_4]^0$ species,[13] cannot be written for $M(SST)_2$ complexes.[16] The close similarity of the first reduction potentials of the latter species suggests that in each case the electron is added to a nearly exclusively ligand-based MO whereas the odd-electron MO in species such as $[NiS_4C_4R_4]^-$ has appreciable metal orbital admixture.[8a]

Results presently at hand demonstrate that dithiotropolone is sufficiently stable to be isolated in substance and that it forms stable bis-chelate complexes whose spectral and electrochemical properties, at least of the Ni, Pd, Pt species, imply a delocalized ground-state description of neutral complexes and monoanions. Finally, it is noted that **3** is a potentially useful intermediate for the synthesis of 1,7-disubstituted cycloheptatrienes by nucleophilic reactions. As a further example, reaction of a 1:2:1 mole ratio of **3**, *p*-toluidine, and sodium ethoxide (EtOH, 80°, 48 hr) yields the known N,N′-*p*-tolylaminotroponeimine[2b] in 46% yield. Further details concerning the synthetic utility of **3** and the structural-electronic properties of dithiotropolone and its metal complexes, together with a comparison of these properties with those of the bisdithiolenes, will be reported subsequently.

Acknowledgment. This research was supported by NSF Grant GP-7576X. We thank Drs. J. P. Fackler and E. L. Muetterties for helpful discussion.

---

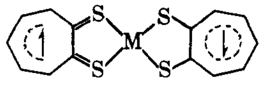
[12] (a) J. P. Fackler, Jr., D. Coucouvanis, J. A. Fetchin, and W. C. Seidel, *J. Am. Chem. Soc.*, **90**, 2734 (1968); (b) M. Bonamico and G. Dessy, *Chem. Commun.*, 483 (1968); (c) C. Furlani and M. L. Luciani, *Inorg. Chem.*, **7**, 1586 (1968).

[13] G. N. Schrauzer and V. P. Mayweg, *J. Am. Chem. Soc.*, **87**, 3585 (1965).

[14] Polarographic data were obtained in DMF solution containing 0.1 *M* $(Bu_4N)(BF_4)$ supporting electrolyte and a rotating platinum electrode; potentials were measured *vs.* sce.

[15] G. N. Schrauzer, *Transition Metal Chem.*, **4**, 299 (1968).

[16] In this connection it is to be noted that, in addition to the ligand-delocalized formulation **6**, other structures, represented collectively by **7**, could also be invoked as possible contributors to the electronic description of $M(SST)_2$ complexes, particularly of those having a planar stereochemistry. The inclusion of such structures would suggest a ground-state VB description related to that of the neutral, diamagnetic bisdithiolenes,[13,15] but with the difference that odd-electron ligand structures need not necessarily arise in the latter cases. The importance of the structures summarized by **7** and the attendant electronic structural similarities between dithiolenes and dithiotropolonates is currently being investigated. The argument[15] that $M(SST)_2$ species will not possess as high electron affinities as the corresponding dithiolene complexes because of the absence of strictly analogous resonance forms receives support from the potentials reported here.



7

[17] National Institutes of Health Predoctoral Fellow, 1968–.

C. E. Forbes,[17] R. H. Holm

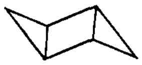
Department of Chemistry, Massachusetts Institute of Technology
Cambridge, Massachusetts 02139

Received September 9, 1968

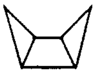
Tricyclo[3.1.0.0^{2,4}]hexane

Sir:

The tricyclo[3.1.0.0^{2,4}]hexane system has received only very limited investigation.[1-4] Moreover, the geometrical isomers of the parent hydrocarbon, **1a** and **1b**, have not been described. We wish to report the synthesis and fundamental characterization of the *trans* isomer **1a**.



1a



1b

Scheme I outlines the synthetic sequence.[5] Treatment of **2**[6] with excess ethereal diazomethane at 0–5° for 3 days provided **3**: 87%; mp 120–121° (from dichloromethane–pentane); $\lambda_{max}^{CH_3OH}$ 323 mμ (ϵ 451) (–N=N–);[7] λ_{max}^{Nujol} 6.45 μ (–N=N–).[7] Compound **3**

---

[1] C. Deboer and R. Breslow, *Tetrahedron Letters*, 1033 (1967).

[2] N. Obata and I. Moritani, *Bull. Chem. Soc. Japan*, **39**, 2250 (1966).

[3] H. H. Stechl, *Chem. Ber.*, **97**, 2681 (1964).

[4] For a review of such highly strained compounds, see D. Seebach, *Angew. Chem. Intern. Ed. Engl.*, **4**, 121 (1965).

[5] Satisfactory elemental analyses were obtained for **1a**, **3**, and **6–8**.

[6] A. Rodgmann and G. F. Wright, *J. Org. Chem.*, **18**, 465 (1953).