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			TABLE I				
Lower Energy Spectral Bands of Cobalt MNT Complexes in Acetone ⁴							
Complex	$\lambda \ (\log \epsilon)$						
$[Co(MNT)_2]^-$		455(3.7)	540 (3.5), sh	790(3.6)	1345(2.9)		
$[Co(MNT)_2C_5H_5N]^{-1}$		453(3.4)		705(3.2)	1100(2.4)		
$[C_0(MNT)_2P(C_6H_5)_3]^{-1}$		495 (3.5)		685(2,7)	1225(3,2)		
$[Co(MNT)_2As(C_6H_5)_3]^{-1}$		530(3.0)		710(2,3)	1330(2.9)		
$[Co(MNT)_{3}]^{3-}$		460 (3.6)		665(2.6)			
$[Co(MNT)_2($	$C_{b}H_{5}N)_{2}]^{-}$	440 (3.4)		700(2.6)			
$[Co(MNT)_2(a)]$	<i>o</i> -phen)] -	428(3.7)		655(2.7)			
$[Co(MNT)_2(o$	tiars)] –	463(3.7)		650(3.2)			

^a Wave length of maxima and shoulders in $m\mu$ (log of molar extinction coefficient follows wave length in parentheses).

of the adduct or by running ligand displacement experiments. All of the compounds are reasonably labile so that equilibration is rapid. Only values for very stable *o*-phen and diars adducts of $Co(MNT)_2^-$ were inaccessible. Apparently, TDT^{2-} increases the stability of the square-planar structure sufficiently to bring the formation constants for the corresponding *o*-phen and diars adducts of $Co(TDT)_2^-$ down to fairly low values (note that only those two ligands yielded adducts with $Co(TDT)_2^-$). Table II contains the values of formation constants for mono adducts with both five- and six-coordination. We can extract the order of ligand affinities for these complexes as diars > *o*-phen > $P(C_6H_5)_3 > C_5H_5N > (C_6H_5)_3As$.

TABLE II

Formation Constants of "Mono Adducts" in Acetone at 25°

Adduct	$\log K_f$
$[Co(MNT)_2As(C_6H_{\delta})_3] =$	2.8
$[Co(MNT)_2(C_5H_5N)]$	3.5
$[Co(MNT)_2P(C_6H_5)_3]^{-1}$	6.1
$[Co(TDT)_2(o-phen)]^-$	1.7
$[Co(TDT)_2(diars)]^-$	2.4

Although usual oxidation state formalism suggests that these complexes be designated "Co(III)," the chemical evidence presented here indicates the difficulties with this designation. Four characteristics of these complexes are not common among Co(III) complexes: (1) stable four-coordinate species, (2) stable five-coordinate species, (3) ready interconvertibility among four-, five-, and six-coordination, and (4) a ligand affinity order with P preferred to N as a donor (the Ahrland, Chatt, and Davies "type B" or Pearson "soft acid" behavior).6 In fact, these properties, taken together, are consistent with the behavior of d⁸ systems and provide substantial support to our earlier electronic structural assignment^{2(a)} of d⁸ (metal) radical anion (ligand) for $Co(TDT)_2^-$ and $Co(MNT)_2^-$. An electronic interpretation of the analogy with d⁸ complexes follows by assuming that at least one bonding electron pair is more nearly localized on the metal than on the ligands.

The question of the structures of the five- and sixcoordinate species is still open. The five-coordinate complexes probably have square-pyramidal geometry. Since the spectra of the six-coordinate species are not typical of octahedral Co(III), an interesting possibility is that the factors which stabilize the square-planar geometry in four-coordination may operate to produce

(6) (a) S. Ahrland, J. Chatt, and N. R. Davies, Quart. Rev. (London),
 12, 265 (1958); (b) R. G. Pearson, J. Am. Chem. Soc., 85, 3533 (1963).

a trigonal prismatic, or at least a strongly trigonally distorted, six-coordinate structure.

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The Structure of Spinochrome M

Sir:

Research on spinochromes, the polyhydroxynaphthoquinone pigments from the spines and tests of sea urchins, has been characterized by an abundance of reported compounds and a paucity of substantiated facts.¹ This situation was dramatically illustrated in the recent communication by Gough and Sutherland,² who established the structure of spinochrome B and proved its identity with no fewer than six previously reported and supposedly different pigments.

Our own suspicion that the chemical literature offered a larger variety of spinochromes than did nature was strengthened when we examined six species of Hawaiian sea urchins in five genera and found that the same pigment occurred as the major pigment in the spines of *Echinometra oblonga* Blainville and *Colobocentrotu's atratus* Linn., and as a minor constituent in the spines of *Tripneustes gratilla* Linn., *Echinothrix diadema* Linn., *E. calamaris* Pallis, and *Diadema paucispinum* Agassiz.

The spines were digested in concentrated hydrochloric acid and the pigments were extracted with ether, washed into aqueous sodium bicarbonate solution under nitrogen, and transferred into benzene after acidification with phosphoric acid. Separation of the pigments was achieved on a column of silica gel (load factor 1000:1), which had been pretreated with 0.5 N hydrochloric acid and dried at room temperature. Elution with benzene removed the major pigment, dark purple needles from methanol, m.p. 192–193°, or 183– 184° as the methanol solvate; yield ca. 0.05% from *E. oblonga* or *C. atratus*. This pigment proved to be identical in all respects (melting point, ultraviolet spectra in three solvents, n.m.r., and thin-layer chromatogram) with an authentic sample of spinochrome M.³

We assigned to spinochrome M structure I (represented here is one of several quinoid tautomers)

R. H. Thomson, "Naturally Occurring Quinones," Butterworths Scientific Publications, London, 1957, pp. 128-140.

⁽²⁾ J. Gough and M. D. Sutherland, Tetrahedron Letters, 269 (1964).

⁽³⁾ We are indebted to Drs. C. Kuroda and M. Okajima for a sample of spinochrome M.

on the basis of the following evidence. Spinochrome



M has the molecular formula $C_{12}H_8O_7$. Anal. Calcd.: C, 54.55; H, 3.05; mol. wt., 264. Found: C, 54.18, 54.37; H, 3.45, 3.19; mol. wt., 264 (mass spectrum⁴). The presence of an acetyl group was demonstrated by a positive iodoform test, a singlet at δ 2.85 in the n.m.r. spectrum,⁵ and strong m/e = 43 and 221 peaks in the mass spectrum. A nucleoid hydrogen was evident from a positive Craven test⁶ and an n.m.r. signal at δ 6.68. A naphthazarin structure was deduced from the high oxygen content and the visible and ultraviolet spectra: λ_{max}^{MeOH} 514 m μ (log ϵ 3.67), 3.17 (4.10), sh 270 (4.14), 251 (4.16); $\lambda_{max}^{0.02}$ M methanolie NaOH 569 m μ (log ϵ 3.80), 469 (3.49), 443 (3.49), 328 (4.28), sh 287 (4.21).

This evidence is equally compatible with I and with its isomer, 2,7-dihydroxy-6-acetylnaphthazarin. Proof of I as the structure of spinochrome M came from the following experiment. Treatment of I with methanolic hydrogen chloride resulted in the loss of the acetyl group and in methylation of two hydroxy groups vielding 2,7-dimethoxynaphthazarin (II), m.p. 235-236°. Anal. Calcd. for $C_{12}H_{10}O_6$: C, 57.60; H, 4.03. Found: C, 57.64; H, 3.62. While this compound was not previously reported, its structure was secured by spectral data and by comparison with its previously unreported isomer, 2,6-dimethoxynaphthazarin (III). Visible and ultraviolet absorption of II showed: λ_{max}^{MeOH} 542 m μ (log ϵ 3.32), 505 (3.53), 477 (3.46), 307 (3.61), 279 (3.60); $\lambda_{\max}^{0.05 \ N \ \text{methanolic KOH}}$ 565 mµ (log ϵ 3.84), 532 (3.86), sh 497 (3.78), sh 319 (3.51), 301 (3.60); n.m.r. spectrum: $C_{2^{\text{-}}}$ and $C_{7^{\text{-}}}OCH_{3},\ \delta$ 3.94; $C_{3^{\text{-}}}$ and C_{6} -H, 6.42; C_{5} -OH, 12.70 or 13.12; C_{8} -OH, 12.70 or 13.12. The nonequivalent chemical shifts for the two strongly hydrogen-bonded OH groups are only compatible with attachment of the two methoxy groups at C_2 and C_7 .

Compound III was prepared from 2,6-dihydroxynaphthalene via the known 1,5-dinitro-2,6-dimethoxy derivative, followed by treatment with sulfur and 30% fuming sulfuric acid according to Charrier and Tocco⁷ in ca. 3% yield. It was isolated from a complex mixture after chromatography on deactivated silica gel, and had m.p. 295–296°, dark red needles from acetone. Anal. Calcd. for C₁₂H₁₀O₆: C, 57.60; H, 4.03. Found: C, 57.80, 57.70; H, 4.01, 4.13. Its ultraviolet spectrum was virtually identical with that of II, but the n.m.r. signals of the two hydrogen-bonded hydroxy protons were now equivalent and appeared at δ 13.07. Remaining n.m.r. signals of III appeared at: C₂- and C₆- OMe, δ 3.93; C₃- and C₇-H, δ 6.36.

Thus I is unambiguously established as the structure of spinochrome M.⁸ Actually in solution spinochrome M cannot be accurately represented by any one species such as I, but must be considered a mixture of several rapidly interconverting tautomers. That this situation holds was seen from the mixture of products obtained on methylation. When I was treated with dimethyl sulfate and potassium carbonate in acetone, one of the products was IV, dark orange needles from chloroform-petroleum ether (b.p. $30-60^{\circ}$), m.p. 224-227°. Anal. Calcd. for C₁₄H₁₂O₇: C, 57.54; H, 4.14. Found: C, 57.60, 57.58; H, 4.54, 4.55. Visible and ultraviolet absorption was shown at: λ_{max}^{MeOH} 450 mµ (log ϵ 3.43), 302 (4.18), 263 (4.07); $\lambda_{\max}^{0.05 \ N \ \text{methanolic KOH}} 460 \ m\mu \ (\log \ \epsilon \ 3.58), \ 377 \ (3.70),$ 302 (4.34), 260 (4.28); n.m.r. spectrum: C₆-COCH₃, $\delta \ 2.83 \ , \ C_7\text{-OCH}_3, \ 3.96 \ ; \ C_2\text{-OCH}_3, \ 3.88 \ ; \ C_3\text{-H}, \ 6.75 \ ;$ C_5 -OH, 17.20; C_8 -OH, 13.50. When, however, I was reacted with diazomethane in ether, one of the products isolated was V, red-orange plates from ether, m.p. 181–182°. Anal. Calcd. for $C_{14}H_{12}O_7$: C, 57.54; H, 4.14. Found: C, 57.28, 56.99; H, 4.52, 4.43. Visible and ultraviolet absorption was evidenced at λ_{\max}^{MeOH} 490 mµ (log ϵ 3.69), 305 (3.86), sh 270 (3.76); $\lambda_{\text{max}}^{0.05~N~\text{methanolic KOH}}$ sh 588 m μ (log ϵ 3.77), 558 (3.98), sh 320 (3.82), 294 (3.89); n.m.r. spectrum: C_4 -OH, δ 12.61 or 13.00; C₃-COCH₃, 2.52; C₈-OH, 12.61 or 13.00; C_7 -OCH₃, 3.92 or 4.05; C_6 -H, 6.20; C_5 -OCH₃; 3.92 or 4.05.



Published ultraviolet spectral data of spinochrome A^{9-11} pointed to the possibility that spinochromes M and A might also be identical although the composition of A is reported to be $C_{12}H_{10}O_8$, differing from M by one molecule of water. A small sample of A^{12} showed identity with M by ultraviolet spectra in three solvents and thin-layer chromatograms in two systems. Lack of material precluded comparison of infrared and n.m.r. spectra. We are planning to isolate a sufficient quantity of A from its original source, the Mediterranean sea urchin *Paracentrotus lividus*, to settle this point beyond doubt.

(8) The Japanese workers arrived at the structure i on the basis of analytical data of the pigment and "derivatives," the isolation of glyoxalic acid



(identified as the 2,4-dinitrophenylhydrazone) upon ozonolysis of a "pentaacetate" [C. Kuroda and M. Okajima, *Proc. Japan Acad.*, **36**, 424 (1960)], and the isolation of what was believed to be 3,4,6-trimethoxyphthalic acid upon oxidation with hydrogen peroxide of the "hexamethyl ether" [M. Okajima, J. Sci. Research Inst. (Tokyo). **53**, 356 (1959)].

(9) E. Lederer and R. Glaser, Compl. rend., 207, 454 (1938).

- (11) T. W. Goodwin and S. Srisukh, Biochem. J., 47, 69 (1950).
- (12) We are grateful to Prof. E. Lederer for this sample.

⁽⁴⁾ We are grateful to Prof. C. Djerassi, Stanford University, for this determination.

⁽⁵⁾ All spectra were produced in deuteriochloroform using tetramethyl-silane as an internal standard (δ 0).

⁽⁶⁾ R. Craven, J. Chem. Soc., 1605 (1931).

⁽⁷⁾ C. Charrier and G. Tocco, Chem. Zentr., 94, 1159 (1923); Gazz. chim. ital., 53, 431 (1923).

⁽¹⁰⁾ R. Glaser and E. Lederer, ibid., 208, 1939 (1939).

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Hydroboration of Ureido-Substituted Olefins¹

Sir:

A research program leading to the synthesis of boron compounds for neutron capture therapy^{2,3} has prompted attempts directed toward the synthesis of nucleic acid bases containing boron as a ring hetero atom. This has resulted in the preparation of several ureidoalkylboronic acids inaccessible by any previously known methods. The synthesis of functionally substituted aliphatic boronic acids has been effected primarily by radical additions of vinylboronic acid derivatives.⁴ The scope of the hydroboration reaction for the synthesis of such compounds is indicated in the work of Brown,⁵ and some examples are realized in this report.

Diborane normally reacts with unhindered olefins to produce trialkylboranes.6 However, when N-vinylurea⁷ (1 mole) was treated with diborane (1.5 moles as BH₃) in tetrahydrofuran at 0° and followed by decomposition of the excess diborane and the intermediate alkylborane with excess methanol, dimethyl β -ureidoethylboronate (Ia), m.p. 65–68°, was formed in 80% yield. Anal. Calcd. for $C_5H_{13}BN_2O_3$: C, 37.54; H, 8.19; B, 6.76; N, 17.52. Found: C, 37.81; H, 8.20; B, 6.85; N, 17.72. This hygroscopic ester afforded the corresponding boronic acid (Ib), m.p. 102-104°, on treatment with water. Anal. Calcd. for C₃H₉BN₂O₃: C, 27.30; H, 6.88; B, 7.64; N, 21.25. Found: C, 27.35; H, 6.92; B, 7.84; N, 21.30. The n.m.r. spectrum of this acid in D₂O showed five exchangeable protons and two triplets (each of two protons, 0.96a nd 3.50, J = 15 c.p.s.), thus establishing the 1:2-disubstituted ethane structure. Both the ester Ia and the acid Ib gave the same derivative II, m.p. 237-238°, when treated with diethanolamine. Anal. Calcd. for $C_7H_{16}BN_3O_3$: C, 41.82; H, 8.02; B, 5.38; N, 20.89. Found: C, 42.10; H, 8.14; B, 5.71; N, 21.10.

(1) This investigation was supported by grants from the John A. Hartford Foundation, Inc., the U. S. Atomic Energy Commission (AT(30-1)3267), and the U. S. Public Health Service (CA 07368).

(2) A. H. Soloway, "Boron Compounds in Cancer Therapy," in "Progress in Boron Chemistry," Vol. 1, Pergamon Press, New York, N. Y., 1964, pp. 203-234.

(3) T. K. Liao, E. G. Podrebarac, and C. C. Cheng, J. Am. Chem. Soc., 86, 1869 (1964), and references cited therein.

(4) D. S. Matteson and W. H. Mah, *ibid.*, **85**, 2599 (1963).

(5) (a) H. C. Brown, "Hydroboration," W. A. Benjamin, Inc., New York,
N. Y., 1962, Chapter 19; (b) H. C. Brown and K. A. Keblys, J. Am. Chem.
Soc., 86, 1791 (1964); (c) H. C. Brown and K. A. Keblys, *ibid.*, 86, 1795 (1964); (d) H. C. Brown and O. J. Cope, *ibid.*, 86, 1801 (1964).

(6) See ref. 5a, chapter 6.

(7) R. Hart, Bull. soc. chim. Belges, 66, 229 (1957)

Using the same conditions, analogous compounds have been obtained from N-propenyl-,⁸ N-cyclo-hexenyl-,⁸ and N-allylurea, in yields ranging from 30 to 90% of theory.



The formation of these monoalkylboronic acid derivatives in such high yields rather than the usual trialkylboron compounds points to the probability of an internally stabilized intermediate such as III being involved. This type of coordination would decrease the reactivity of the monoalkylborane to further hydroboration of unsaturated centers. Thus, the reaction would terminate at this stage. The utilization of one mole of "hydride"^{5b,c} per mole of olefin in the hydroboration of certain unsaturated chlorides and tosylates^{5b} and the facile reduction of unsaturated esters^{5c} where such cyclic entities can occur lend support to this type of coordinated monoalkylborane intermediate.

The extension of this work to other functionally substituted olefins bearing atoms which can coordinate with the introduced borane moiety in five-, six- or sevenmembered intermediates is underway in these laboratories. In this manner, it is expected that the reaction will terminate at the monoalkylborane stage, thus permitting the synthesis of other substituted alkylboronic derivatives. The further interaction of the boronic acid moiety with the functional group may permit the synthesis of new boron heterocycles of potential pharmacological interest.

Acknowledgment.—The authors wish to thank William H. Sweet, M.D., Chief of the Neurosurgical Services at the Massachusetts General Hospital, for his interest and encouragement.

(8) D. N. Butler and A. H. Soloway, unpublished work. These ureas were prepared by the method used by Hart (see ref. 7) for the synthesis of N-vinylurea and satisfactory analytical data have been obtained for these compounds.

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Dihalomethylenation of Protonic Acids with Phenyl(trihalomethyl)mercury Compounds

Sir:

The dihalomethylenation by phenyl(trihalomethyl)mercury compounds of C-H, Si-H, and Ge-H bonds,¹ as well as the halogenation of Sn-H bonds by such mercurials,² have been reported. We have extended our studies of the reactions of phenyl(trihalomethyl)-

⁽¹⁾ D. Seyferth and J. M. Burlitch, J. Am. Chem. Soc., 85, 2667 (1963).

⁽²⁾ D. Seyferth, H. D. Simmons, Jr., and L. J. Todd, J. Organometal. Chem., in press.