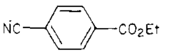
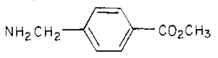
Table II. Reductions with Co_2B/TAB

substrate	conditions[a]	product (yield, %)
PhCN	2 equiv TAB, 3 h	$PhCH_2NH_2$ (75)
$PhCH_2CN$	2 equiv TAB, 7 h	$PhCH_2CH_2NH_2$ (88)
$CH_3(CH_2)_4CN$	2 equiv TAB, 2.5 h	$CH_3(CH_2)_5NH_2$ (81)
	4 equiv TAB, 12.5 h	 (75)
$PhCONH_2$	2 equiv TAB, 3 h	NR[b]
$PhCH{=}CHCO_2CH_3$	2 equiv TAB, 3 h	$PhCH{=}CHCO_2CH_3$ (75)
$CH_3(CH_2)_5C{\equiv}CH$	2 equiv TAB, 2 h	$\left.\begin{matrix}\text{octene}\\ \text{octane}\end{matrix}\right\}$ (25)[c] octyne (75)

[a] All reactions were run with 1 equiv of Co_2B at reflux in CH_3OH under N_2. [b] No reaction. [c] Yield determined by GC.

nificant part in the reduction of nitriles and carboxamides by this system.

Although fresh supernatant alone from $NaBH_4/CoCl_2$ mixtures did not reduce benzonitrile, some benzylamine could be produced even from aged supernatant in the presence of Co_2B. Thus a mixture of $NaBH_4$ (10 mmol) with $CoCl_2$ (2 mmol) in CH_3OH (6 mL) was stirred for 50 min until gas evolution had subsided. Benzonitrile (1 mmol) was then added, and workup afforded benzylamine (18% after 15 min; 25% after 5 h), apparently formed by residual $NaBH_4$ in a Co_2B-assisted process.

Consistent with this hypothesis, benzonitrile treated with prewashed Co_2B and then with $NaBH_4$ in CH_3OH afforded benzylamine in 85% yield.[24] Similar results were obtained with both 6-week-old and recycled samples of the boride. In fact, an efficient catalytic reduction was devised by utilizing 10 mol % of Co_2B with portionwise addition of $NaBH_4$ until TLC analysis indicated complete consumption of starting material. Cobalt boride/$NaBH_4$ rapidly converted methyl cinnamate to methyl hydrocinnamate (85%)[3] and 1-octyne to octane (83%). The latter transformation may be a catalytic hydrogenation;[19] the former clearly is not, nor is it a reaction of $NaBH_4$ alone. Prior poisoning of the catalyst with ethylenediamine[25] dramatically inhibited all these reductions. Moreover $NaBH_3CN$ could not replace $NaBH_4$ as the hydride source. Table I summarizes representative reductions.

At present our results cannot distinguish whether free $NaBH_4$ or some other, more complex reducing agent formed directly on the boride surface is the actual "hydride" donor. Among such possibilities are multinuclear, bridged borohydrides, heterogeneous Co–H complexes,[26] or even transient quantities of highly reactive, surface-generated BH_3. The chemistry of Co_2B with amine boranes was explored to evaluate this last prospect. These reducing agents are stable at ambient temperature but thermally dissociate into free BH_3.[27] When *tert*-butylamine–borane (TAB), a reagent normally inert to nitriles, was combined with benzonitrile and an equivalent of Co_2B, benzylamine was produced in high yield. Alkenes and alkynes were reduced more slowly in this system than with $NaBH_4/CoCl_2$ (Table II). Moreover a large excess of reducing agent was unnecessary since TAB decomposed only sluggishly during reduction. This new reaction should prove useful in many complex synthetic transformations.

Whatever their mechanism, these amine–borane reductions are not catalytic in the boride and must involve some complex surface phenomena besides ordinary chelation that deserves further study in aprotic media. New heterogeneous organometallic reactions under those conditions will be the subject of a future report. For the moment, our mechanistic findings should be of interest with respect to other transition-metal-assisted hydride reductions where the corresponding borides are formed in situ.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

Registry No. 1, 83462-98-0; **2**, 83462-99-1; Co_2B, 12045-01-1; *t*-$BuNH_2{\cdot}BH_3$, 7337-45-3; $NaBH_3CN$, 25895-60-7; PhCN, 100-47-0; $PhCH_2CN$, 140-29-4; $NaBH_4$, 16940-66-2; $CoCl_2$, 7646-79-9; $PhCONH_2$, 55-21-0; $PhCH{=}CHCO_2CH_3$, 103-26-4; $CH_3(CH_2)_5C{\equiv}CH$, 629-05-0; $PhCH_2NH_2$, 100-46-9; $PhCH_2CH_2NH_2$, 64-04-0; $PhCH_2CH_2CO_2CH_3$, 103-25-3; $CH_3(CH_2)_4CN$, 628-73-9; $CH_3(CH_2)_5NH_2$, 111-26-2; octane, 111-65-9; ethyl 4-cyanobenzoate, 7153-22-2; methyl 4-(aminoethyl)benzoate, 18469-52-8.

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[24] This yield is undoubtedly higher; controls showed some loss of benzylamine due to volatility and water solubility.

[25] Brown, C. A.; Ahuja, V. K. *J. Chem. Soc., Chem. Commun.* **1973**, 553.

[26] If Co–H species are involved, earlier experiments with tritiated $NaBH_4$ indicate very little exchange of hydrogen ligands with the medium.[11,12]

[27] (a) Lane, C. F. *Aldrichemica Acta* **1973**, *6*, 21. (b) Andrews, G. C.; Crawford, T. C. *Tetrahedron Lett.* **1980**, *21*, 693.

Dihydroxamate Analogues of Rhodotorulic Acid and an Exceptional Dimer: Preparation and Crystal Structure of $Fe_2[i\text{-}C_3H_7N(O)C({=}O)({-}CH_2{-})_5\text{-}C({=}O)N(O)\text{-}i\text{-}C_3H_7]_2(\mu\text{-}OCH_3)_2$

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The siderophores are low molecular weight chelating agents that are produced by microbes to solubilize and transport ferric ion to the cell membrane.[1,2] The hydroxamate group $[HON(R_1)(C({=}O))R_2]$ is one of the most common functional groups found in siderophores produced by molds, fungi, and yeasts. The compounds are predominantly trihydroxamic acids that form extremely stable 1:1 complexes with Fe^{3+}. Rhodotorulic acid (RA, **1a**, Figure 1) is unusual among the hydroxamate siderophores in that it is a dihydroxamic acid and is thus unable to satisfy the preferred octahedral coordination geometry of Fe^{3+} by the formation of a simple 1:1 complex. We have shown that RA forms a dimeric complex in solution of stoichiometry Fe_2RA_3.[3] Unfortunately there is no experimental evidence to distinguish between proposed structure **1b** with three bridging hydroxamate ligands and alternative structure **1c**, which possesses only a single bridging ligand. Furthermore, we have been unable thus far to isolate single crystals of Fe_2RA_3 for an X-ray structural analysis.

In an effort to lend support to the triply bridged dimeric structure proposed for ferric rhodotorulate, a series of model ligands, $i\text{-}C_3H_7N(OH)C({=}O)({-}CH_2{-})_nC({=}O)N(OH)\text{-}i\text{-}C_3H_7$ (n = 3–6, 8, 10) were prepared,[4] and their coordination chemistry with Fe^{3+} was examined. Molecular models indicate that by varying the chain length between the functional groups, the distance between the metal centers in the triply bridged dimers may be systematically varied from approximately 5 to 12 Å. It was of interest to determine what effect the chain length would have on the chemical and physical properties of the dimeric complexes as the distance between the paramagnetic iron centers is adjusted.

In aqueous solution the synthetic dihydroxamate ligands form complexes with Fe^{3+} that are analogous to the RA complex over the entire range of chain lengths.[5] The formation constants per

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[1] Neiland, J. B., Ed. "Microbial Iron Metabolism"; Academic Press: New York, 1974.

[2] Neilands, J. B. "Inorganic Biochemistry"; Eichorn, G., Ed.; Elsevier: New York, 1973.

[3] Carrano, C. J. Raymond, K. N. *J. Am. Chem. Soc.* **1978**, *100*, 5371.

[4] Smith, W. L.; Raymond, K. N. *J. Am. Chem. Soc.* **1980**, *102*, 1252.

[5] Analytical data are consistent with $Fe_2L_3{\cdot}H_2O$ when isolated from solutions with Fe:L = 2:3. Solid complexes appear to be polymeric; however molecular weight measurements (gel partition chromatography in H_2O and MeOH) are consistent with a dimeric formulation.

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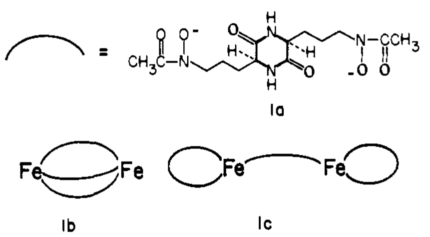

Figure 1. Structure of rhodotorulic acid (**1a**) and the possible structures for dimeric ferric dihydroxamate complexes (**1b** and **1c**), where the arc represents the tetradentate dihydroxamate dianion (notice that each end of the arc representing the ligand is actually a bidentate chelate ring, with metal binding through the carbonyl and nitrogen oxygen atoms).

ferric ion are ~10^{31}, and within experimental error are identical with that determined for Fe_2RA_3.[6] Indeed, the synthetic ligands facilitate iron transport in the yeast *Rhodotorula pilimanae*, from which rhodotorulic acid is isolated. Transport with the synthetic ligands occurs via two processes: active transport and diffusion.[7]

Since the Fe–Fe distance can be continuously varied in these compounds by changing the number of bridging methylene units, the magnetic iinteraction of the two Fe centers has been examined. In frozen methanol, relaxation effects in the EPR and Mössbauer spectra suggest a dipolar interaction between the ferric ions for the shorter chains (n = 3, 4, 6), thus supporting the proposed triply bridged structure **1b**. The magnitude of this interaction increases with decreasing chain length; the ferric ions are noninteracting in the complexes with RA and the synthetic ligands with n = 8, 10. This trend in Fe–Fe interaction is also observed in the electrochemical properties of the ferric complexes.[8]

Investigation of the visible spectra of the dihydroxamate complexes in methanol show that for the n = 5 complex an anomalous species is formed which is not a tris-hydroxamate complex. The visible spectrum has a λ_{max} of 414 nm (ϵ 2100), whereas the other complexes exhibit a λ_{max} of 425 nm (ϵ 3300), which is characteristic of ferric tris-hydroxamate complexes. The low extinction coefficient of the n = 5 complex suggests that loss of a dihydroxamate ligand occurs upon dissolution in methanol. The EPR spectrum (MeOH, 115 K) displays a single resonance at g = 4.3, characteritic of rhombically distorted ferric ion.[9] The signal is extremely weak relative to those obtained for the other ferric dihydroxamate complexes. The Mössbauer spectrum (MeOH, 4.2 K) is a simple quadrupole doublet as opposed to the magnetically split spectra observed for the other ferric dihydroxamate complexes. These results imply strong coupling between the iron centers, possibly through an oxygen bridge. Finally, the room-temperature magnetic suusceptibility is ~4.8 μ_B indicating that the two iron centers are antiferromagnetically coupled.[10]

The anomalous n = 5 ferric complex is isolated from methanol containing an equimolar ratio of ferric ion to dihydroxamic acid. Elemental analysis of the crystalline material obtained is consistent with the formulation $Fe_2L_2(OCH_3)_2$ (**2**).[11]

Excellent single crystals of **2** form from methanol solution at room temperature as red-orange plates in monoclinic space group $P2_1/n$[12] with a = 11.453 (1) Å, b = 14.986 (2) Å, c = 11.948 (1) Å, and β = 119.05 (1)°. The measured density of 1.32 g cm^{-3} is consistent with the calculated value of 1.331 g cm^{-3} for two molecules of **2** per unit cell. The structure was solved by standard heavy-atom procedures and refined by full-matrix least-squares methods.[13] At convergence, R = 0.027 and R_w = 0.039.[14]

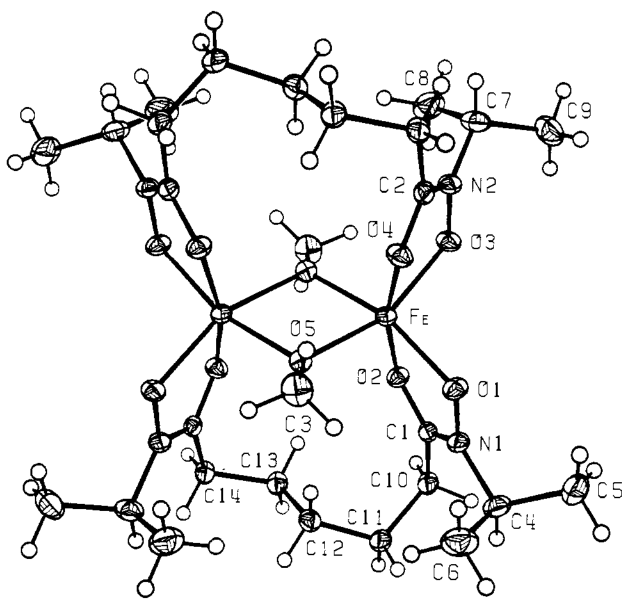

Figure 2. Perspective drawing of **2**. Non-hydrogen atoms are shown as ellipsoids of 30% probability, and hydrogen atoms as spheres of radius 0.1 Å.

The complex is dimeric and possesses rigorous C_i symmetry and, as shown in Figure 2, essentially C_{2h} symmetry. The two dihydroxamate ligands bridge the two Fe^{3+} ions such that the two carbonyl oxygen (O_c) atoms occupy opposite positions about Fe^{3+} (O_c–Fe–O_c = 165°); hence **2** is analogous to the trans isomer of the tris-hydroxamate complexes.[15] The coordination sphere about the Fe^{3+} ions is completed by the two methoxide oxygen atoms, which bridge the metals in a slightly asymmetric manner [Fe–O_{Me} = 1.999 (1) Å, Fe′–O_{Me} = 2.006 (1) Å].[16] The Fe···Fe′ distance is 3.168 (1) Å and the Fe–O–Fe′ angle is 104.58 (5)°. The presence of this four-membered Fe_2O_2 ring accounts for the antiferromagnetic behavior, which is suggested by the Mössbauer and magnetic susceptibility data. The planarity of the four-atom hydroxamate moieties (Fe^{3+} deviates by 0.35 and 0.49 Å from these mean planes) and other aspects of the coordination geometry of **2** are fully consistent with similar features of previously reported metal–hydroxamate complexes.[17,18]

In addition to explaining the changes in the visible, Mössbauer, and EPR spectra and magnetic susceptibility of the n = 5 complex upon dissolution in methanol, the structure of **2** bears upon an understanding of the structure of the naturally occurring diiron complex, ferric rhodotorulate. That is, the bridging dihydroxamate **2** provides additional support for the formulation of Fe_2RA_3 as tribridged species **1b** rather than monobridged species **1c**. Why this dimer is observed in solution or in the solid state only for the five methylene bridge ligand (but not for n = 4 or 6, for example) is not clear from either models or simple conformational differences.

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(10) Magnetic susceptibilities were determined in MeOH by using the NMR technique. Values calculated for the other ferric complexes ($n \neq 5$) were ~ 5.9 μ_B [$\mu_{s.o.}Fe(III)_{hs}$ = 5.92].

(11) Anal. Calcd for $Fe_2L_2(OCH_3)_2$: C, 46.80; H, 7.52; N, 7.80; Fe, 15.60. Found: C, 46.77; H, 7.52; N, 7.76; Fe, 15.7. Mp 233 °C dec; IR ν 2807 cm^{-1} (C–H, OCH_3); in the deuterated complex ν 2050 cm^{-1} (C–D, OCD_3); calcd 2059 cm^{-1}.

(12) An alternative setting of space group $P2_1/c$ with equivalent positions $\pm(x, y, z; {}^1/_2 + x, {}^1/_2 - y, {}^1/_2 + z)$.

(13) Experimental procedures followed and computer programs used are presented elsewhere: Eigenbrot, C. W., Jr.; Raymond, K. N. *Inorg. Chem.* **1982**, *21*, 2653.

(14) The error indices are $R = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_w = [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2}$.

(15) Raymond, K. N.; Abu-Dari, K.; Sofen, S. R. *ACS Symp. Ser.* **1980**, *119*, 133.

(16) The ratio of the difference in the Fe–O(methoxide) bond lengths to their rms deviation is 3.53 and therefore is significant in accordance with the criterion presented previously: Cruickshank, D. W. J. *Acta Crystallogr.* **1949**, *2*, 65.

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Registry No. 1a, 18928-00-2; **2**, 83380-29-4.

Supplementary Material Available: Table of atomic positional parameters with estimated standard deviations (1 page). Ordering information is given on any current masthead page.

Tetracyanoquinodimethane-Modified Electrodes

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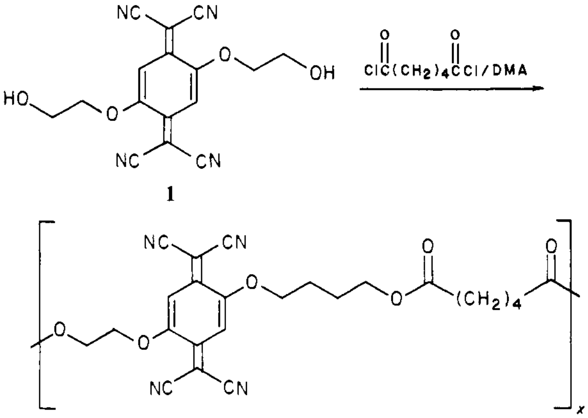
Herein we report on the preparation and characterization of modified electrodes based on the widely studied tetracyanoquinodimethane (TCNQ) acceptor molecule. The electrodes are fabricated in the usual way[1] by adsorption on a platinum-coated quartz substrate, by using novel TCNQ oligomers in which the electron-exchange sites are incorporated in the molecular backbone. In contrast to other acceptor film modified electrodes, which are water and air sensitive[2] or complicated by slow charge transfer between redox sites,[3] these TCNQ electrodes are stable upon repeated electrochemical cycling between the zero and −1 oxidation states in aqueous electrolytes, and the amount of charge accepted by the films is proportional to film thickness over the range 10–1000 nm. Thus these electrodes complement donor polymer film electrodes such as the poly(vinylferrocene)[4] and tetrathiafulvalene[5] (TTF) electrodes in that cathodic intercalation of cations into the TCNQ film is readily achieved from aqueous solutions.



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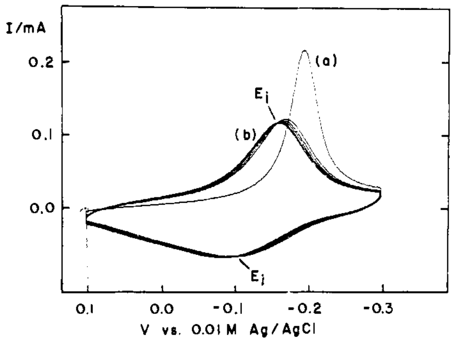

Figure 1. Cyclic voltammogram of a 800-nm $(TCNQ)_x$ film at 0.02 V/s in aqueous 0.5 M $NaClO_4$, 0.01 M NaCl: (a) first sweep; (b) repetitive cycles (E_i isopotential points).

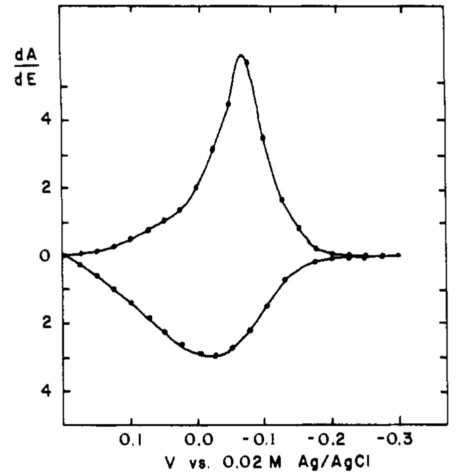

Figure 2. Derivative cyclic voltabsorptometry of a 800-nm $(TCNQ)_x$ film at 0.001 V/s in aqueous 0.5 M $LiClO_4$, 0.02 M LiCl; points are experimental; λ 735 nm; dA/dE given in absorbance units per volt.

The $(TCNQ)_x$ was synthesized by treatment of the dioxydiethanol TCNQ monomer (**1**) of Hertler[6] with a stoichiometric amount of adipoyl chloride in *N,N*-dimethylacetamide (DMA) at room temperature for more than 24 h. A light red-purple powder was obtained after the reaction mixture was poured into ethanol.[7] The average molecular weight of the resulting $(TCNQ)_x$ oligomeric mixture was estimated to be 2200 by the "universal" gel permeation chromatography method of Grubisic et al.[9]

Cyclic voltammograms of solutions of $(TCNQ)_x$ in acetonitrile revealed the expected quasi-reversible reduction waves

$$(TCNQ)_x \overset{xe^-}{\rightleftharpoons} (TCNQ^-)_x \overset{xe^-}{\rightleftharpoons} (TCNQ^{2-})_x \tag{2}$$

($E_{1/2}{}^{0/-} = 0.06$ and $E_{1/2}{}^{-/2-} = -0.39$ V vs. SCE) for noninteracting electron-transfer sites, in agreement with the reversible waves observed for the monomer. Peak heights for the $(TCNQ)_x$ waves were attenuated due to the smaller diffusion coefficients of the oligomeric species.[10,11] The absorption spectrum of the neutral $(TCNQ)_x$ featured two peaks at λ_{max} 408 nm (log ε 5.06) and 430 (log ε 5.06), while the electrogenerated $(TCNQ^-)_x$ polyanion spectrum showed bands at λ_{max} 445 nm (log ε 4.30), 660 (log ε 3.38), 728 (log ε 3.92), and 812 (log ε 4.20). These data are consistent with the corresponding spectra of the substituted monomeric TCNQ[12] and its radical anion.[13]

Films that were spin-coated (solvent: tetrahydrofuran) onto platinum-on-quartz substrates and baked for 2–3 min at 130–140 °C were studied in aqueous electrolytes. These films were found to be insoluble in water in both the zero and −1 oxidation states

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(7) Reaction times from 25 h to approximately 1 week have been employed for this and related polymerizations. (In a typical procedure, 0.42 g of $(TCNQ)_x$ was realized from the first crop (53% yield).) Condensation polymerizations of this type are thoroughly treated by Morgan.[8]

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(12) We find λ_{max} 412 and 432 nm for **1**, while Hertler reports λ_{max} 412 and 342 nm in ref 6.

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