

N-O, 180° to 174.29°; final N-N bond length, 1.44 Å.

All angles were varied linearly along the reaction coordinate; bond lengths remained constant.

Note Added in Proof. Recently, another coordination compound, $[\text{PPh}_4][\text{ReF}_2\text{Cl}_2(\text{N}_2\text{S}_2)]$, bearing the N_2S_2 ligand has been prepared and

its crystal structure has been established.²⁴ The S-S bond length in this compound (2.429 Å) is slightly shorter than those published previously.⁴ It indicates that the potential energy surface for S-S bond length variations is quite shallow.

(24) Dehnicke, K. Personal communication.

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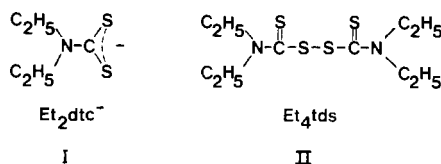
Exchange and Other Reactions Associated with Zinc(II) Dithiocarbamate Oxidation and Reduction Processes Observed at Mercury and Platinum Electrodes in Dichloromethane

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The electrochemical behavior of zinc(II) dithiocarbamate complexes ($\text{Zn}(\text{RR}'\text{dtc})_2$) has been investigated at both platinum and mercury electrodes and compared with that of the analogous cadmium complexes ($\text{Cd}(\text{RR}'\text{dtc})_2$). Oxidation at mercury electrodes in the presence of $\text{M}(\text{RR}'\text{dtc})_2$ ($\text{M} = \text{Zn}, \text{Cd}$) consists of three reversible processes. The first of these involves an exchange reaction between metal(II) dithiocarbamate and electrode mercury: $\text{M}(\text{RR}'\text{dtc})_2 + \text{Hg} \rightarrow \text{Hg}(\text{RR}'\text{dtc})_2 + \text{M}^{2+} + 2\text{e}^-$ ($\text{M} = \text{Zn}, \text{Cd}$). This reaction is mediated by formation of a bimetallic cation $[\text{MHg}(\text{RR}'\text{dtc})_2]^{2+}$, small amounts of which were detected on the synthetic time scale associated with bulk electrolysis experiments at a mercury-pool electrode. The remaining two oxidation processes arise from formation of $\text{Hg}(\text{RR}'\text{dtc})_2$, which is in equilibrium with the bimetallic complex at the electrode surface. At platinum electrodes, oxidation processes are observed at much more positive potentials than at mercury electrodes and yield the thiuram disulfide complexes $[\text{MR}_2\text{R}'_2\text{tds}]^{2+}$. However, for $\text{Zn}(\text{RR}'\text{dtc})_2$, the more positive oxidation potential ($E_p(\text{Zn}) = 1.6 \text{ V}$ vs $E_p(\text{Cd}) = 1.3 \text{ V}$ vs Ag/AgCl) leads to further oxidation to give an unidentified product. The oxidation products formed at platinum electrodes in bulk electrolysis experiments interact strongly with electrode mercury to give polarographic responses that are similar to those for the oxidation products formed at mercury electrodes, demonstrating the considerable lability of the zinc- (and cadmium-) mercury dithiocarbamate interactions. Reduction processes for $\text{Zn}(\text{RR}'\text{dtc})_2$ are less affected by the choice of electrode material than are the oxidation processes. At both platinum and mercury electrodes, the major reduction process occurs at very negative potentials (approximately -2 V vs Ag/AgCl) and yields elemental zinc or zinc amalgam, respectively, and free dithiocarbamate. At mercury electrodes, a minor additional reduction pathway involving exchange between $\text{Zn}(\text{RR}'\text{dtc})_2$ and electrode mercury was noted. The analogous process for $\text{Cd}(\text{RR}'\text{dtc})_2$ provides the major route for reduction of the cadmium complexes at mercury electrodes. Surprisingly, no reduction of $\text{Cd}(\text{RR}'\text{dtc})_2$ is observed at platinum electrodes.

The electrochemical behavior of $\text{Hg}(\text{RR}'\text{dtc})_2$ ($\text{RR}'\text{dtc} =$ dialkyl dithiocarbamate; see structure I)^{1,2} and $\text{Cd}(\text{RR}'\text{dtc})_2$ ³ complexes has been described in some detail, particularly at mercury electrodes. In contrast, while the chemically related $\text{Zn}(\text{RR}'\text{dtc})_2$



compounds are used widely in the chemical industry^{4,5} and a great deal is known about their general chemical reactivity and physical chemistry, little is known of their redox properties. Electrochemical oxidation of $\text{Zn}(\text{Et}_2\text{dtc})_2$ in acetone (0.1 M Et_4NClO_4) at a platinum electrode has been shown to give a poorly defined, chemically irreversible response at a very positive potential.⁶ The product(s) was (were) not isolated, but one was postulated to be a thiuram disulfide (Et_4tds , structure II) complex of zinc(II), $[\text{Zn}(\text{Et}_4\text{tds})]^{2+}$, on the basis of extrapolation from the observation that related species are formed via chemical (halogen) oxidation

of zinc(II) dithiocarbamates.⁷ That is, oxidation at solid electrodes has been assumed to be ligand based. The only other report on electrochemical oxidation processes concerns the polarographic behavior of $\text{Zn}(\text{pyrrdtc})_2$ at positive potentials in methyl isobutyl ketone (0.1 M Bu_4NClO_4).⁸ A single oxidation wave at -0.05 V vs the saturated calomel reference electrode was shown to be a chemically reversible two-electron step. The proposed mechanism involved an exchange reaction between the zinc complex and electrode mercury to form $\text{Hg}(\text{pyrrdtc})_2$ and zinc(II) ions. This is analogous to the mechanism reported for $\text{Cd}(\text{RR}'\text{dtc})_2$.³

The reduction of $\text{Zn}(\text{RR}'\text{dtc})_2$ complexes at mercury electrodes has been addressed briefly.^{8,9} In methyl isobutyl ketone⁸ and dimethylformamide⁹ a reduction process occurs at very negative potentials, which has been proposed as a two-electron step leading to the formation of zinc amalgam and free dithiocarbamate ion. However, as in the oxidation studies cited above, controlled-potential electrolysis experiments were not undertaken so that conclusive evidence regarding the products (and intermediates) of redox processes is not available.

The purpose of this study is to present a more complex view of the electrochemical behavior of $\text{Zn}(\text{RR}'\text{dtc})_2$ complexes at both mercury and platinum electrodes and to compare results with known and new information now available on electrochemical processes for the corresponding cadmium(II) dithiocarbamate complexes. The detailed investigations reveal hitherto unknown complexities and the formation of a new class of bimetallic complexes.

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Table I. Differential-Pulse Polarographic Data^{a,b} for the Oxidation Processes Observed in the Presence of Zn(RR'dtc)₂ and Hg(RR'dtc)₂ in Dichloromethane (0.1 M Bu₄NClO₄) at 20 °C

R	R'	E_p^{ox}, V^c		
		process 1	process 2	process 3
Me	Me	0.335	0.495 (0.485)	0.610 (0.605)
Et	Et	0.320	0.470 (0.450)	0.650 (0.640)
<i>n</i> -Pr	<i>n</i> -Pr	0.335	0.450 (0.450)	0.660 (0.650)
<i>i</i> -Pr	<i>i</i> -Pr	0.355	0.450 (0.455)	0.660 (0.630)
<i>n</i> -Bu	<i>n</i> -Bu	0.365	0.470 (0.455)	0.670 (0.665)
<i>i</i> -Bu	<i>i</i> -Bu	0.395	0.495 (0.490)	0.695 (0.715)
<i>c</i> -Hx	<i>c</i> -Hx	0.350	0.460 (0.435)	0.640 (0.625)
	pip ^d	0.350	0.460 (0.435)	0.600 (0.585)
	pyrr ^e	0.330	0.400 (0.400)	0.575 (0.560)

^a E_p^{ox} = peak potential for oxidation process. Data for the corresponding Hg(RR'dtc)₂ oxidation processes are included in parentheses.

^b Dropping-mercury electrode; drop time 0.5 s; pulse amplitude 50 mV.

^c Potential vs Ag/AgCl. ^d pip represents piperidine-1-carbodithioate.

^e pyrr represents pyrrolidine-1-carbodithioate.

Experimental Procedures

Materials. All solvents and reagents used were of analytical reagent grade purity. The electrochemical supporting electrolytes Bu₄NClO₄ and Et₄NClO₄, obtained from South Western Analytical Chemicals, Austin, TX, were dried and recrystallized from dichloromethane/diethyl ether prior to use.

Preparations. M(RR'dtc)₂ (M = Cd, Zn) complexes were prepared according to previously reported methods,³ which involved stirring together stoichiometric amounts of sodium hydroxide, carbon disulfide, and the appropriate secondary amine in water followed by the addition of metal(II) nitrate. The resulting precipitate was filtered out, dried, and purified by Soxhlet extraction into dichloromethane.

Instrumentation. Voltammetric measurements were made with a Princeton Applied Research Corp. (PAR) (Princeton, NJ) Model 174A polarographic analyzer with a dropping-mercury electrode or a polished platinum disk working electrode. For experiments with a rotating platinum disk electrode, a Metrohm Model 628-10 drive unit and Model 628-50 electrode assembly were used. A platinum wire served as the auxiliary electrode, while the reference electrode was Ag/AgCl (saturated LiCl/EtOH) separated from the test solution by a salt bridge containing the appropriate solvent. The half-wave potential for the (C₅H₅)₂Fe⁺/(C₅H₅)₂Fe redox couple was measured frequently to provide an internal check on the stability of the reference electrode. Oxidation of 10⁻³ M ferrocene had a half-wave potential of +0.500 V vs Ag/AgCl at both mercury and platinum working electrodes. Unless otherwise stated all measurements were made at 20 °C with 0.1 M supporting electrolyte present.

Controlled-potential electrolysis experiments were performed at either a mercury-pool or a platinum-gauze working electrode with a PAR Model 173 potentiostat/galvanostat in conjunction with a PAR Model 179 digital coulometer. The platinum-gauze auxiliary electrode was isolated from the test solution via a salt bridge, and the reference electrode was the same as that used for voltammetry.

Results and Discussion

(a) Oxidation Processes in the Presence of Zn(RR'dtc)₂ at Mercury Electrodes. Three dc (direct current) polarographic oxidation waves are observed in dichloromethane at the dropping-mercury electrode in the presence of 5 × 10⁻⁴ M Zn(RR'dtc)₂. These waves are referred to as processes 1, 2, and 3, and their limiting currents are in the ratio 2:1:1, respectively. Process 1 (least positive) was accompanied by a prewave, as also observed by Ichimura et al.⁸ in their study of Zn(pyrrdte)₂ (chemical symbols defined in Table I) in methyl isobutyl ketone. They examined this phenomenon in some detail and were able to show that this response is due to product adsorption. However, processes 2 and 3 were not reported in ref 8.

In the case of some substituents, processes 1 and 2 were incompletely resolved, and in other cases, processes 2 and 3 were distorted by adsorption, which made the assignment of accurate dc half-wave potentials difficult. Better resolution was obtained in the differential-pulse polarographic mode, and polarographic data obtained from this technique are collected in Table I. Differential-pulse peak potentials for the oxidation potentials are similar to the dc half-wave potentials. Oxidative cyclic voltammograms were also recorded at a slowly growing mercury-drop

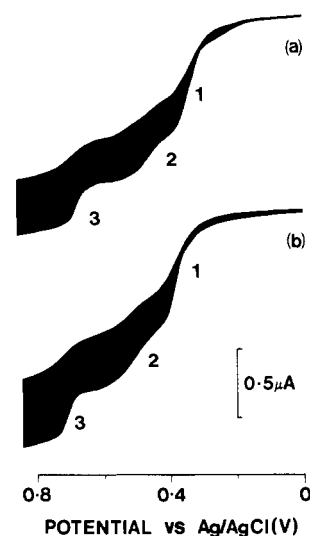


Figure 1. Dc polarograms for the oxidation processes observed in the presence of 5 × 10⁻⁴ M (a) Zn(*n*-Pr₂dte)₂ and (b) Cd(*n*-Pr₂dte)₂ in dichloromethane (0.1 M Bu₄NClO₄) with drop time 0.5 s and temperature 20 °C.

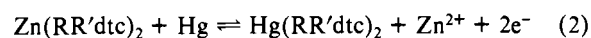
electrode in the presence of Zn(RR'dtc)₂ compounds. A high degree of chemical reversibility was observed for each of the three processes under conditions of cyclic voltammetry at mercury electrodes.

Examination of polarograms for Hg(RR'dtc)₂ complexes reveals that processes 2 and 3 for Zn(RR'dtc)₂ occur at dc half-wave potentials and differential-pulse peak potentials (Table I) very similar to those found for the two oxidation processes observed in the presence of the corresponding mercury complex. In previous studies^{1,2} it was shown that each oxidation process observed at mercury electrodes in the presence of Hg(RR'dtc)₂ is a one-electron step generating mercury-rich cations and involves oxidation of the mercury electrode rather than oxidation of the complex. Comparison of the total limiting currents for the three Zn(RR'dtc)₂ processes is approximately twice that for the two mercury processes. Assuming that the zinc and mercury complexes have similar diffusion coefficients, process 1 for the zinc complex is therefore defined as a two-electron step.

These data for oxidation processes at mercury electrodes in the presence of Zn(RR'dtc)₂ complexes are similar to those observed in the presence of the corresponding cadmium complexes.³ This is well illustrated by Figure 1, which shows the oxidative dc polarograms in the presence of Zn(*n*-Pr₂dte)₂ (Figure 1a) and Cd(*n*-Pr₂dte)₂ (Figure 1b) at the same concentration in dichloromethane. The data for polarographic oxidation of Cd(RR'dtc)₂ were described by eq 1.³ In view of the strong similarity



of the responses, an analogous eq 2 is formulated for the zinc



complexes. This represents an exchange reaction between electrode mercury and Zn(RR'dtc)₂, which forms the mercury dithiocarbamate complex and zinc(II). The reaction is rapid, since the response for process 1 is diffusion-controlled. Processes 2 and 3 are therefore the one-electron-oxidation processes observed at mercury electrodes in the presence of Hg(RR'dtc)₂ and which² involve the formation of mercury-rich cations such as [Hg₃(Et₂dte)₄]²⁺.

If eq 2 is correct and Zn²⁺ is soluble on the dc polarographic time scale, then it follows that a plot of dc potential of dc polarograms versus the current function log [(i_d - i)/i²] should be linear with a slope of -29 mV at 20 °C. While the plots were linear, slopes were found to be in the range of -32 to -41 mV for the different complexes. Thus, for most of the zinc dithiocarbamate complexes, the observed responses differ somewhat from theoretical expectations based on eq 2. This indicates that

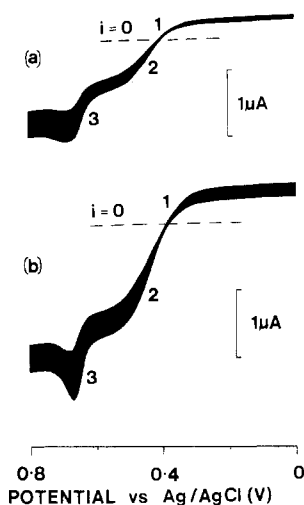


Figure 2. Dc polarograms (drop time 0.5 s) observed after exhaustive controlled-potential oxidative electrolysis (process 1) at 20 °C at a mercury-pool electrode in dichloromethane (0.1 M Bu_4NClO_4) in the presence of (a) 1.3×10^{-3} M $\text{Zn}(\text{Et}_2\text{dtc})_2$ and (b) 1×10^{-3} M $\text{Cd}(\text{Et}_2\text{dtc})_2$.

eq 2 may be an oversimplification of oxidation process 1. Distortion due to uncompensated solution resistance was ruled out after noting that such effects were totally absent in the oxidative polarogram recorded for ferrocene (a known reversible one-electron-oxidation process) under the same conditions.

In order to obtain more complete details on the mechanism of the oxidation, controlled-potential electrolysis experiments were carried out at a mercury-pool electrode. If, on the synthetic time scale, zinc(II) perchlorate as an insoluble salt and mercury(II) dithiocarbamate were formed as predicted from eq 2, it would be expected that process 1 would disappear after electrolysis but processes 2 and 3 would remain. In the case of $\text{Zn}(\text{Et}_2\text{dtc})_2$, electrolysis on a 1.3×10^{-3} M solution in dichloromethane with the potential set at 0.38 V vs Ag/AgCl resulted in the passage of 2.0 ± 0.1 faradays/mol, confirming the formulation of process 1 as a two-electron step. The resulting solution was cloudy due to the formation of a white precipitate. This was filtered out and shown to be $\text{Zn}(\text{ClO}_4)_2$ by comparison of the polarographic response in aqueous 0.1 M KNO_3 with that for an authentic sample. The remaining dichloromethane solution contained mainly $\text{Hg}(\text{Et}_2\text{dtc})_2$ at close to the expected concentration (1.3×10^{-3} M), and the dc polarogram of the solution after electrolysis is shown in Figure 2. Interestingly, the zero of current (response for solvent and supporting electrolyte alone) for this dc polarogram passes through the rising portion of the first wave and not at the foot. That is, careful inspection of Figure 2 reveals that this wave is in fact composed of a small reductive component at the potential of process 1 plus the major oxidative component due to the formation of $\text{Hg}(\text{Et}_2\text{dtc})_2$ (process 2). This implies that the product (or products) of process 1 on the long time scale include a dichloromethane soluble species. This is rather unexpected.

The dc polarogram in Figure 2b is for a solution of $\text{Cd}(\text{Et}_2\text{dtc})_2$ subjected to the same bulk electrolysis procedure at a mercury-pool electrode. The response is almost identical with that for the zinc complex (Figure 2a). Again, the solution contains mainly $\text{Hg}(\text{Et}_2\text{dtc})_2$. However, as for the zinc complex a small quantity of a soluble species that is the primary product of oxidation process 1 is formed. The formula of this species can be inferred from the identity of the products, which form on the longer time scale: $\text{Hg}(\text{Et}_2\text{dtc})_2$ and Zn^{2+} or Cd^{2+} . In view of the above evidence, eq 1 and 2 can be rewritten as in eq 3a and 3b to give a more

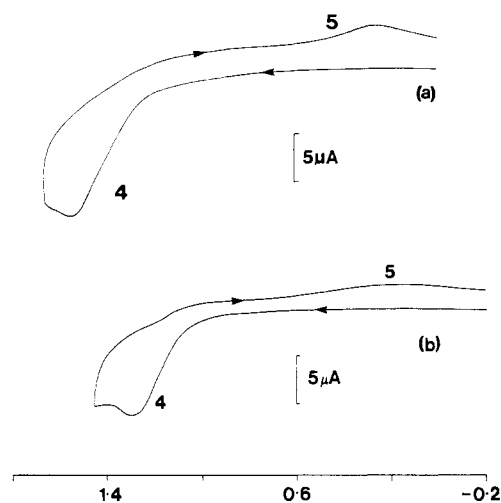
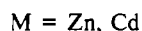
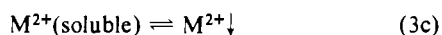
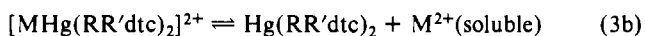


Figure 3. Cyclic voltammograms (scan rate 500 mV s^{-1}) at a platinum electrode for oxidation of 5×10^{-4} M (a) $\text{Zn}(\text{pipdtc})_2$ and (b) 5×10^{-4} M $\text{Cd}(\text{Et}_2\text{dtc})_2$ in dichloromethane (0.1 M Bu_4NClO_4) at 20 °C.

Table II. Cyclic Voltammetric Data^a at a Platinum Electrode (Scan Rate 500 mV s^{-1}) for Oxidation of $\text{Zn}(\text{RR}'\text{dtc})_2$ Complexes in Dichloromethane (0.1 M Bu_4NClO_4) at 20 °C

R	R'	$E_p^{\text{ox}}, \text{V}^b$ process 4	$E_p^{\text{red}}, \text{V}^b$ process 5
Me	Me	1.60	0.30
Et	Et	1.60	0.32
<i>n</i> -Pr	<i>n</i> -Pr	1.60	0.25
<i>i</i> -Pr	<i>i</i> -Pr	1.56	0.15
<i>n</i> -Bu	<i>n</i> -Bu	1.70	0.30
<i>i</i> -Bu	<i>i</i> -Bu	1.75	0.25
<i>c</i> -Hx	<i>c</i> -Hx	1.70	0.35
	pip	1.56	0.26
	pyrr	1.55	0.35

^a E_p^{ox} = oxidation peak potential; E_p^{red} = reduction peak potential observed on the reverse scan. ^b Potential vs Ag/AgCl. Chemical symbols are as in Table I.

specific representation of oxidation process 1. The bimetallic cations are only stable in solution under the above specified electrochemical conditions and could not be isolated. On removal of the solvent, the bimetallic complex produces the highly stable mercury dithiocarbamate complex and the metal(II) cation. In dichloromethane and the presence of the electrolyte, the metal cation forms the very insoluble metal(II) perchlorate, which may well be the driving force for the reaction given in eq 3b. While the formula of the bimetallic cation is written in its simplest form as $[\text{MHg}(\text{RR}'\text{dtc})_2]^{2+}$, its structure is unknown and the actual species may be of higher molecular weight or an equilibrium mixture of a range of species.

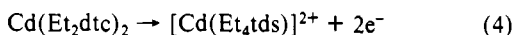
(b) Oxidation Processes for $\text{M}(\text{RR}'\text{dtc})_2$ ($\text{M} = \text{Zn, Cd}$) at Platinum Electrodes. A typical cyclic voltammogram for oxidation of $\text{Zn}(\text{RR}'\text{dtc})_2$ in dichloromethane at a platinum electrode is shown in Figure 3a. A single, poorly defined oxidation process 4 is seen at very positive potentials, and peak potentials lie in the range 1.55–1.8 V vs Ag/AgCl (Table II). Process 4 is chemically irreversible, and a peak (process 5) is seen on the reverse (reductive) scan at 0.15–0.35 V vs Ag/AgCl (Table II), which is broad in shape. Figure 3b shows the response for a cadmium dithiocarbamate complex ($\text{Cd}(\text{Et}_2\text{dtc})_2$) under the same conditions. The response is similar to that for $\text{Zn}(\text{pipdtc})_2$ (Figure 3a) although oxidation (process 4) occurs at less positive potentials for the cadmium complex ($E_p^{\text{ox}} = 1.3 \text{ V vs Ag/AgCl}$; cf. $E_p^{\text{ox}}(\text{Zn}(\text{Et}_2\text{dtc})_2) = 1.6 \text{ V vs Ag/AgCl}$).

In order to determine the number of electrons transferred in process 4, controlled-potential electrolysis experiments at a platinum-gauze electrode were conducted. Electrolysis at a platinum-gauze electrode of a dichloromethane solution of $\text{Cd}(\text{Et}_2\text{dtc})_2$ at +1.4 V vs Ag/AgCl resulted in the passage of 2.0 ± 0.1 faradays/mol. The solution was faintly cloudy due to the for-

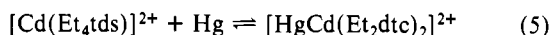
mation of a small amount of fine white precipitate, which was shown to be Cd(ClO₄)₂ by reductive polarography of this isolated product in aqueous 0.1 M KNO₃.

The voltammetry of the solution electrolyzed at a platinum electrode showed no response in the region of the original oxidation process. The only voltammetric response at a platinum electrode observed after this bulk electrolysis experiment was a broad reduction process centered at -0.15 V vs Ag/AgCl. The potential of this process coincided with process 5 (see Figure 3a) observed in cyclic voltammograms, so the same species appear to be produced on the short time scale of voltammetry and long time scale of controlled-potential electrolysis.

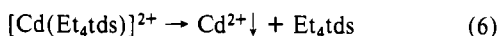
The dc polarographic response observed at a mercury electrode after bulk electrolysis at the platinum electrode provides additional information. Processes 1-3 are all present, although the current for process 1 is less than the sum of the currents for processes 2 and 3. Importantly, the response for the solvent and supporting electrolyte alone (*i* = 0) passes through the midpoint of processes 1 and 2, which is also the case after oxidative electrolysis of Cd(Et₂dtc)₂ at a mercury electrode. Results indicate that, in the presence of a mercury electrode, the same product is formed as is the case after bulk electrolysis at mercury electrodes. An explanation of the results at a platinum electrode is that the product at platinum electrodes reacts rapidly with electrode mercury to form [HgCd(RR'dtc)₂]²⁺, the postulated product of electrolysis at mercury electrodes. The large positive oxidation potential observed at a platinum electrode for Cd(RR'dtc)₂ implies that the product of the reaction is a strong oxidant that could be expected to react readily with elemental mercury. Since the formation of a cadmium(III) dithiocarbamate species is entirely unprecedented, then ligand-based oxidation of Cd(RR'dtc)₂ to form a species featuring coordinated thiuram disulfide is more likely, as in eq 4. This species, a thiuram disulfide complex of



cadmium(II), must then react with mercury according to eq 5.



The species [Cd(Et₄tds)]²⁺ generated after electrolysis at a platinum electrode is not completely stable, liberating cadmium as Cd(ClO₄)₂ during the course of the electrolysis. Equation 6 is therefore applicable on longer time scale experiments.



The cadmium cation is identified as the insoluble perchlorate salt. The other product, tetraethylthiuram disulfide, displays polarographic behavior identical with that for Hg(Et₂dtc)₂ due to rapid reaction with mercury at the electrode surface. This has been demonstrated by recording the polarogram of an authentic sample of Et₄tds, which is indistinguishable from that observed for Hg(Et₂dtc)₂. Thus, despite the fact that some [Cd(Et₄tds)]²⁺ dissociates, as evidenced by formation of insoluble Cd(ClO₄)₂, the total current (processes 1-3) is not attenuated, despite the loss of cadmium due to the precipitation process. Rather, the current for process 1 decreases while that for processes 2 and 3 increases via formation of Et₄tds, which is equivalent to Hg(dtc)₂ at the mercury electrode surface.

Bulk oxidative controlled-potential electrolysis also was carried out on Zn(RR'dtc)₂ compounds at platinum electrodes but was complicated by the very positive oxidation potentials for these complexes that are close to the solvent oxidation limit in dichloromethane. Therefore, the applied potential was set at a value corresponding to the rising portion of the cyclic voltammetric oxidation process to minimize overlap with the solvent oxidation process. Under these conditions, the bulk electrolysis proceeded with the passage of 3.8 ± 0.2 faradays/mol. No insoluble Zn(ClO₄)₂ was observed after this electrolysis. Cyclic voltammetry at a platinum electrode after electrolysis showed that the peak for process 4 was no longer present, indicating that all Zn(RR'dtc)₂ had been consumed. In fact, the only response observed was a reduction peak at the potential for process 5, which shows that the product(s) of controlled-potential electrolysis is (are) the same

as that formed on the much shorter time scale of cyclic voltammetry. It is also apparent from examination of such cyclic voltammograms that reduction according to process 5 does not regenerate Zn(Et₂dtc)₂, as a response corresponding to formation of this complex is not observed on the reverse (oxidative) scan of this cyclic voltammetric experiment.

The oxidative dc and differential-pulse polarograms at a mercury electrode for Zn(RR'dtc)₂ after bulk electrolysis at a platinum electrode exhibit three waves, which resemble those for the starting material (processes 1-3). The dc polarographic limiting currents for the three waves are approximately in the ratio of 2:1:1, but the total limiting current has been reduced to around 30% of that observed at a mercury electrode in the presence of Zn(RR'dtc)₂ before electrolysis. The responses have also been shifted to more positive potentials. The cyclic voltammograms at a hanging mercury drop demonstrate that all three processes are chemically reversible. The coulometric and voltammetric data obtained after bulk electrolysis experiments suggest that Zn-(RR'dtc)₂ complexes undergo a more extensive ligand oxidation than the cadmium analogue and form species that cannot be quantitatively converted to the product of electrolysis at a mercury electrode. That is, while oxidation of Cd(RR'dtc)₂ at a platinum electrode leads to quantitative formation of a thiuram disulfide complex that can interact with electrode mercury to give responses at the same potentials as those for the starting material, the oxidation products of Zn(RR'dtc)₂ have been oxidized further, to a point where quantitative recovery of the metal and ligand is impossible. An alternative product giving rise to process 5 has therefore been formed during the oxidation process.

If a species such as R₂R'₂bitt²⁺ is formed via a four-electrode oxidation process as indicated by the coulometric data, then elemental sulfur should also have been formed as a product.¹⁰ However, elemental sulfur was not detected in the electrolyzed solution. The very positive potential of process 4 means that some of the charge transferred may have been devoted to oxidation processes associated with the solvent. After electrolysis at a platinum electrode, the solution was pale green, with no evidence of the formation of insoluble Zn(ClO₄)₂. Thus, all the zinc remains in solution as a coordinated complex. In a chlorinated solvent such as dichloromethane, species such as chloride and radicals may be generated by electrochemical oxidation and these products may react with the initially formed product of zinc dithiocarbamate oxidation. The product of oxidation at a platinum electrode is not stable in the presence of water, and shaking with aqueous 0.1 M KNO₃ resulted in the dichloromethane solution losing its green coloration. A polarographic study of both aqueous and nonaqueous phases showed that all the zinc had been transferred to the aqueous layer via this solvent extraction process. That is, the oxidation waves akin to processes 1-3 were totally removed in the dichloromethane phase and the expected amount of zinc(II) was determined in the aqueous phase. Cyclic voltammetry at a platinum electrode of the dichloromethane solution showed that reduction process 5 remained unchanged after the extraction process, indicating that this process is not associated with any zinc-based species and therefore must be due to a ligand-based product or solvent-based product. Thus, although the oxidation process for Zn(RR'dtc)₂ appears similar to that for Cd(RR'dtc)₂ on the cyclic voltammetric time scale, bulk oxidative electrolysis showed that the two processes are substantially different on the longer time scale. The difference appears to stem mainly from the greater difficulty of oxidation of the zinc complexes that results in the generation of other species after initial formation of [Zn(R₂R'₂tds)]²⁺.

(c) Reduction Processes for Zn(RR'dtc)₂ at Mercury and Platinum Electrodes. The chemically irreversible reduction responses observed near the solvent limit for a 5 × 10⁻⁴ M solution of Zn(pyrrdtc)₂ at mercury and platinum electrodes in dichloromethane are shown in Figure 4. Reduction peak potentials obtained from differential-pulse polarograms are collected in Table III. The values are only slightly dependent on the organic

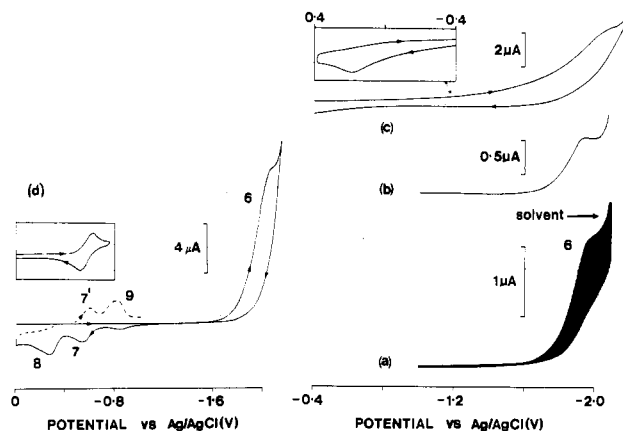


Figure 4. Electrochemical responses observed at 20 °C for the reduction of 5×10^{-4} M $\text{Zn}(\text{pyrrdtc})_2$ in dichloromethane (0.1 M Bu_4NClO_4) for (a) dc polarogram (drop time 0.5 s), (b) differential-pulse polarogram (drop time 0.5 s, pulse amplitude -50 mV), (c) cyclic voltammogram (scan rate 500 mV s^{-1}) at a platinum electrode (insert is the extended potential range), and (d) cyclic voltammogram (scan rate 500 mV s^{-1}) at a mercury electrode (insert is the response for $\text{Hg}(\text{pyrrdtc})_2$).

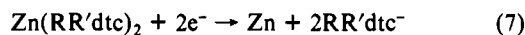
Table III. Data for the Electrochemical Reduction of $\text{Zn}(\text{RR}'\text{dtc})_2$ Complexes at Mercury and Platinum Electrodes in Dichloromethane (0.1 M Bu_4NClO_4) at 20 °C^a

R	R'	cyclic voltammetry ^c	
		$E_p^{\text{red}}, \text{V}^d$	$E_p^{\text{ox}}, \text{V}^d$
Me	Me	-1.96	-2.10
Et	Et	-1.93	-1.95
<i>n</i> -Pr	<i>n</i> -Pr	-1.95	-2.00
<i>i</i> -Pr	<i>i</i> -Pr	-1.92	-2.30
<i>n</i> -Bu	<i>n</i> -Bu	-1.90	-2.00
<i>i</i> -Bu	<i>i</i> -Bu	-1.95	-2.00
<i>c</i> -Hx	<i>c</i> -Hx	-1.92	-2.00
	pip	-1.96	-1.98
	pyrr	-1.94	-2.10

^a E_p^{red} = reduction peak potential; E_p^{ox} = oxidation peak potential observed on the reverse scan. ^b Dropping-mercury electrode (drop time 0.5 s, pulse amplitude -50 mV). ^c Platinum electrode (scan rate 500 mV s^{-1}). ^d Potential vs Ag/AgCl. ^e Overlaps with solvent limit. Chemical symbols are as in Table I.

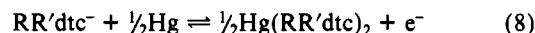
substituent (R/R') group and the electrode material. The location of the $\text{Zn}(\text{RR}'\text{dtc})_2$ reduction process in the region of solvent reduction made it impossible to carry out reductive controlled-potential electrolysis experiments at either electrode material. However, information on the products of reduction could be obtained from a detailed study of the cyclic voltammetric behavior of $\text{Zn}(\text{RR}'\text{dtc})_2$ complexes.

In addition to process 6, the cyclic voltammogram at a platinum electrode for reduction of $\text{Zn}(\text{pyrrdtc})_2$ (Figure 4c) also shows an oxidation peak at 0.18 V vs Ag/AgCl on the reverse scan. This peak potential corresponds to the potential at which oxidation of the free dithiocarbamate ligand (in this case pyrrdtc⁻) takes place, as verified by addition of $(\text{Bu}_4\text{N})(\text{pyrrdtc})$ to the same solution and by observing the peak height for this process increase in height. Analogous behavior was also observed for other $\text{Zn}(\text{RR}'\text{dtc})_2$ complexes (Table III), which confirms that reduction process at platinum electrodes follows eq 7.

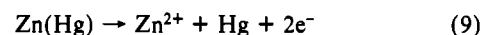


Reduction process 6 at mercury electrodes occurs at potentials similar to those at platinum electrodes and follows a reaction analogous to that shown in eq 7 except that a zinc amalgam rather than zinc metal is formed at the mercury electrode. This is confirmed by examination of cyclic voltammograms recorded at a single drop of a slowly growing dropping-mercury electrode for the irreversible reduction of a solution of $\text{Zn}(\text{RR}'\text{dtc})_2$ (Figure 4d). On the first and subsequent oxidative scans, and the second reductive scan, several new, well-defined electrochemical processes

appear at the mercury electrode (now referred to as processes 7, 7', 8, and 9). These processes are not present at platinum electrodes. Processes 7 and 7' form a chemically reversible couple, and their potentials vary with the organic R/R' group. It was readily shown that process 7 arises from the liberation of free dithiocarbamate, which then gives rise to the process summarized in simplified form in eq 8. This reaction has been studied in detail¹ and a close correspondence of peak potential is observed.



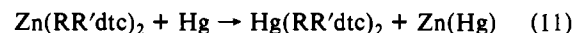
Process 8 is an irreversible oxidation process that occurs at -0.28 V vs Ag/AgCl, and its position (potential) does not vary by more than 20 mV for the entire range of $\text{Zn}(\text{RR}'\text{dtc})_2$ complexes. It can be assigned to the oxidation process for a zinc amalgam, since a 5×10^{-4} M zinc amalgam electrode produced an oxidation essentially identical with the process 8 observed in cyclic voltammograms after reduction of $\text{Zn}(\text{RR}'\text{dtc})_2$. The zinc amalgam is oxidized according to eq 9. Reduction of $\text{Zn}(\text{RR}'\text{dtc})_2$ therefore



takes place at a mercury electrode as in eq 10 with the formation of zinc amalgam.



At mercury electrodes, the reaction given in eq 10 is mediated to a minor extent by a process present in the cyclic voltammogram of $\text{Zn}(\text{Me}_2\text{dtc})_2$ at a slowly growing dropping-mercury electrode. When the potential is held at 0.0 V vs Ag/AgCl for 3 s, small responses are recorded for processes 7' and 9 independently of the occurrence of process 6. Thus, eq 11 can be written to describe the existence of a slow exchange reaction for all $\text{Zn}(\text{RR}'\text{dtc})_2$ compounds.



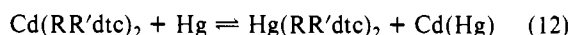
An exchange reaction analogous to that given in eq 11 was noted for cadmium dithiocarbamate complexes under the same conditions.³ However, in this case, exchange occurred to a much greater extent with the result that formation of mercury dithiocarbamate was appreciable, even on the time scale of dc polarography (drop time 0.5 s). For reduction of $\text{Cd}(\text{RR}'\text{dtc})_2$ at mercury electrodes, the observed response consisted of a series of reduction waves with the total current approaching that of the diffusion-controlled wave for the two-electron reduction to elemental mercury for the same concentration of mercury dithiocarbamate.

In contrast with $\text{Zn}(\text{RR}'\text{dtc})_2$, exchange is a relatively minor event on the cyclic voltammetric time scale and direct reduction, according to eq 10, is the major route. This is somewhat surprising since, as noted for $\text{Cd}(\text{RR}'\text{dtc})_2$, such an exchange process offers a relatively facile pathway for reduction ($E_{1/2}^{\text{red}}(\text{Hg}(\text{RR}'\text{dtc})_2) \approx -0.7$ V vs Ag/AgCl, $E_{1/2}^{\text{red}}(\text{Zn}(\text{RR}'\text{dtc})_2) \approx -1.9$ V). A major barrier to rapid exchange may lie in the electrochemically irreversible formation of zinc amalgam, which is contrasted with the electrochemically reversible formation of a cadmium amalgam.³

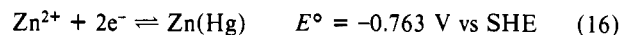
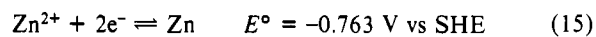
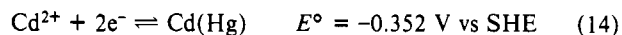
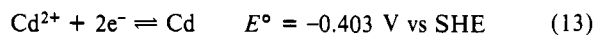
Previous studies on the polarographic reduction of $\text{Zn}(\text{RR}'\text{dtc})_2$ complexes have been carried out in a range of solvents.^{8,9} No substantial solvent effects on the reduction process appear to be present.

While reduction of $\text{Zn}(\text{RR}'\text{dtc})_2$ is essentially unaffected by change from a mercury electrode to a platinum electrode, the behavior of the cadmium analogues is greatly affected by the change to the platinum surface. In fact, no reduction response at all was observed for any $\text{Cd}(\text{RR}'\text{dtc})_2$ complex at platinum electrodes in the accessible potential region (to approximately -2 V vs Ag/AgCl). This is a surprising result since polarographic studies at a mercury electrode in a range of solvents^{3,9} have uniformly demonstrated that $\text{Cd}(\text{RR}'\text{dtc})_2$ complexes are more easily reduced, relative to other metal dithiocarbamates such as $\text{Zn}(\text{RR}'\text{dtc})_2$. Special significance may be attached to the fact that, at a platinum electrode, the metal (cadmium) must be reduced to the free elemental state, rather than the amalgam state

that ensues at mercury electrodes, and provides a more facile path to reduction via eq 12.



That is, the differences in reduction behavior for the two metal systems at the two electrode surfaces also may be partly accounted for by considering the standard reduction potentials for these metals¹¹ at metal and amalgamated electrode surfaces.



These values are for measurements in aqueous solution, relative to the potential of the standard hydrogen electrode. Values in dichloromethane are unknown but can be presumed to be parallel. If this is the case, then the formation of zinc amalgam from zinc(II) is more difficult than formation of cadmium amalgam from cadmium, as is the case in other solvents. However, interestingly the reduction of metal(II) to the amalgam state is favored over production of the elemental state for cadmium, but this is not the case for zinc. Thus, thermodynamic as well as kinetic data offer some explanation as to (a) the insensitivity of the $\text{Zn}(\text{RR}'\text{dte})_2$ reduction potential to electrode material and (b) the relative ease of reduction of $\text{Cd}(\text{RR}'\text{dte})_2$ at mercury relative to platinum electrodes. Therefore, it seems that both kinetic and thermodynamic factors may account for the unexpected difficulty in reduction of the cadmium complexes at platinum electrodes.

Conclusion

The electrochemistry of $\text{Zn}(\text{RR}'\text{dte})_2$ complexes is similar in many respects to that of the cadmium analogues. This is particularly true under oxidative conditions. Polarographic oxidation processes observed at mercury electrodes in the presence of Zn -

$(\text{RR}'\text{dte})_2$ occur at almost the same potential as for the cadmium complexes and in a similarly narrow potential range. The results show that a bimetallic dithiocarbamate cation of the kind $[\text{MHg}(\text{RR}'\text{dte})_2]^{2+}$ is produced as an intermediate in the oxidation process observed at mercury electrodes. In both cases, the formation of the stable $\text{Hg}(\text{RR}'\text{dte})_2$ complexes and the metal perchlorate salt was noted on the longer time scale of controlled-potential electrolysis experiments. At platinum electrodes, $\text{Zn}(\text{RR}'\text{dte})_2$ compounds are more difficult to oxidize than $\text{Cd}(\text{RR}'\text{dte})_2$. Both species are assumed to be initially oxidized to $[\text{M}(\text{R}_2\text{R}'_2\text{tds})]^{2+}$ complexes. For $\text{Zn}(\text{RR}'\text{dte})_2$, the ultimate oxidation product is a more highly ligand oxidized species that may possibly be connected with the solvent oxidation processes that overlap with the zinc oxidation process.

Reduction processes for $\text{Zn}(\text{RR}'\text{dte})_2$ are similar at both platinum and mercury electrodes. This is in sharp contrast to the case for $\text{Cd}(\text{RR}'\text{dte})_2$, for which a reduction process at a platinum surface was not even observed. At mercury electrodes, reduction processes for the cadmium complexes were seen to be significantly dependent on the presence of an exchange reaction to form the mercury dithiocarbamate complexes and metal amalgam.³ While such behavior was also observed for $\text{Zn}(\text{RR}'\text{dte})_2$ complexes, its contribution to the reduction process was relatively small on the polarographic time scale, and the major irreversible two-electron-reduction response at very negative potentials was almost identical with that found at platinum electrodes.

Registry No. $\text{Zn}(\text{Me}_2\text{dte})_2$, 137-30-4; $\text{Zn}(\text{Et}_2\text{dte})_2$, 14324-55-1; $\text{Zn}((n\text{-Pr})_2\text{dte})_2$, 15694-56-1; $\text{Zn}((i\text{-Pr})_2\text{dte})_2$, 14434-68-1; $\text{Zn}(n\text{-Bu})_2\text{dte})_2$, 136-23-2; $\text{Zn}((i\text{-Bu})_2\text{dte})_2$, 36190-62-2; $\text{Zn}(c\text{-Hx})_2\text{dte})_2$, 35091-69-1; $\text{Zn}(\text{pip})\text{dte})_2$, 13878-54-1; $\text{Zn}(\text{pyrr})\text{dte})_2$, 40211-68-5; $\text{Hg}(\text{Me}_2\text{dte})_2$, 15415-64-2; $\text{Hg}(\text{Et}_2\text{dte})_2$, 14239-51-1; $\text{Hg}((n\text{-Pr})_2\text{dte})_2$, 21439-57-6; $\text{Hg}((i\text{-Pr})_2\text{dte})_2$, 21439-56-5; $\text{Hg}((n\text{-Bu})_2\text{dte})_2$, 21439-58-7; $\text{Hg}((i\text{-Bu})_2\text{dte})_2$, 79001-48-2; $\text{Hg}(c\text{-Hx})_2\text{dte})_2$, 21439-59-8; $\text{Hg}(\text{pip})\text{dte})_2$, 21439-62-3; $\text{Hg}(\text{pyrr})\text{dte})_2$, 41060-60-0; $\text{Cd}((n\text{-Pr})_2\text{dte})_2$, 55519-99-8; $\text{Cd}(\text{Et}_2\text{dte})_2$, 14239-68-0; Hg , 7439-97-6; Pt , 7440-06-4; $[\text{ZnMe}_4\text{tds}]^{2+}$, 124381-29-9; $[\text{ZnEt}_4\text{tds}]^{2+}$, 124381-30-2; $[\text{Zn}(n\text{-Pr})_4\text{tds}]^{2+}$, 124381-31-3; $[\text{Zn}(i\text{-Pr})_4\text{tds}]^{2+}$, 124381-32-4; $[\text{Zn}(n\text{-Bu})_4\text{tds}]^{2+}$, 124381-33-5; $[\text{Zn}(i\text{-Bu})_4\text{tds}]^{2+}$, 124381-34-6; $[\text{Zn}(c\text{-Hx})_4\text{tds}]^{2+}$, 124381-35-7; $[\text{Zn}(\text{pip})_4\text{tds}]^{2+}$, 124381-36-8; $[\text{Zn}(\text{pyrr})_4\text{tds}]^{2+}$, 124381-37-9; Zn , 7440-66-6; zinc amalgam, 11146-96-6.

(11) *CRC Handbook of Chemistry and Physics*, 62nd ed.; Weast, R. C., Ed.; CRC Press: Boca Raton, FL, 1981.

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Preparation and Reactions of Bis(aminoboryl) Oxides¹

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Bis(aminoboryl) oxides (=1,3,2-diboroxanes) of the general type $[(\text{CH}_3)_2\text{N}]_2\text{RBOBR}[\text{N}(\text{CH}_3)_2]$ (**1a**, $\text{R} = \text{N}(\text{CH}_3)_2$; **1b**, $\text{R} = \text{C}_2\text{H}_5$; **1c**, $\text{R} = \text{C}_6\text{H}_5$) have been prepared by the controlled hydrolysis of (dimethylamino)chloroboranes, $(\text{CH}_3)_2\text{NBClR}$. The compounds rearrange at elevated temperatures in an equilibrium reaction with the formation of boroxins, $(\text{RBO})_3$, and bis(dimethylamino)boranes, $[(\text{CH}_3)_2\text{N}]_2\text{BR}$, a reaction that can also be used for the preparation of compounds of type **1**. However, irreversible decomposition of **1** by organyl group migration to yield (dimethylamino)diorganylboranes, $(\text{CH}_3)_2\text{NBR}_2$, and B, B', B'' -tris(dimethylamino)boroxin, $[(\text{CH}_3)_2\text{NBO}]_3$, has also been observed at elevated temperatures. Transamination reactions of **1** have been utilized for the preparation of additional bis(aminoboryl) oxides, e.g., $(\text{C}_4\text{H}_8\text{N})(\text{C}_6\text{H}_5)\text{BOB}(\text{C}_6\text{H}_5)(\text{NC}_4\text{H}_8)$ (**2**, $\text{C}_4\text{H}_8\text{NH} = \text{pyrrolidine}$), as well as for the synthesis of heterocyclic systems containing an annular BOB group, e.g., $\text{O}(\mu\text{-RBNR}')_2\text{CX}$ (**4**, $\text{X} = \text{O}, \text{S}$) from the reaction of **1** with (thio)ureas, $(\text{R}'\text{HN})_2\text{CX}$. The heterocycle $\text{O}(\mu\text{-C}_2\text{H}_5\text{BNCH}_3)_2\text{BC}_2\text{H}_5$ (**3**) was obtained from the reaction of **1b** with $\text{C}_2\text{H}_5\text{B}(\text{NHCH}_3)_2$. Transamination of **1** with amides or aminoborination reactions with isocyanates gave bicyclic systems (by intramolecular coordination) of the amidoborane, $(\text{R}'\text{CONR}'')\text{RBOBR}(\text{NR}''\text{COR}')_2$ (**8**), or ureidoborane, $[(\text{CH}_3)_2\text{NCONR}']\text{RBOBR}[\text{NR}'\text{CON}(\text{CH}_3)_2]$ (**6**), type, respectively. A triply bridged species containing both three- and four-coordinate boron, $\text{RB}(\mu\text{-NHCH}_3)(\mu\text{-OBRO})(\mu\text{-NCH}_2\text{CHNCH}_3)\text{BR}$ (**10**), was obtained from the reaction of **1c** with *N*-methylformamide.

Introduction

Although a variety of diboryl oxides (=1,3,2-diboroxanes) of the general type $\text{RR}'\text{BOBR}'$ are known,² the preparation of only

one species has been described where one of the boron substituents is a simple amino group, i.e., $[(\text{CH}_3)_2\text{N}](\text{C}_6\text{H}_5)\text{BOB}(\text{C}_6\text{H}_5)[\text{N}(\text{CH}_3)_2]$.^{3,4} Furthermore, $[(\text{CH}_3)_2\text{N}]\text{HBOBH}[\text{N}(\text{CH}_3)_2]$ has

(1) Boron-Nitrogen Compounds. 123 (K.N.). Part 122: Komorowski, L.; Niedenzu, K. *Z. Naturforsch.*, in press. Parts of the experimental work were extracted from ref 3.

(2) *Gmelin Handbook of Inorganic Chemistry*; Springer Verlag: Berlin, 1977; New Supplement Series, Vol. 48, Boron Compounds 16, pp 73-100.