spectrum of $Li[Cr(edta)]$, which has edta coordinated as a sexidentate ligand, exhibits only one Raman band between 450 and 500 cm^{-1}. In contrast, $[Cr(Hedta)(H_2O)]$, in which the edta is coordinated in a quinquedentate fashion, shows two bands in this region. These observations further support the solution structure of the chromium(III)–edta complex discussed above. The splitting of the Raman band in the quinquedentate complex may be due to the lack of symmetry.

Wheeler and Legg[12] observed continuous shifts, in the positions of the deuteron resonances for deuterated Cr(III)–edta, when the pH of the solution was increased from 0.9 to 10.6. These continuous shifts in the ^2H NMR were explained as arising from the rapid equilibria of I ↔ II and II ↔ III as compared to the NMR time scale. On the other hand, the Raman spectra at pH values near the two pK_a's for the chromium(III)–edta system are easily explained by the superposition of the spectra of the coexisting species. This fact is undoubtedly due to the short time scale of the Raman scattering phenomenon.

Registry No. $Li[Cr^{III}(edta)]$, 76547-63-2; $[Cr^{III}(Hedta)(H_2O)]$, 15955-81-4.

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A New Class of Substituted Amine–Boranes: The Amine–(α-Cyanoorgano)boranes

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The general synthesis and chemistry of amine–cyanoboranes, $R_{3-x}NH_x{\cdot}BH_2CN$ (x = 0–3), have been reported by Spielvogel.[1,2] The trimethylamine derivative shows potent antiarthritic, antihypolipidemic, and antitumor activity on rodents[3] and is the precursor to $(CH_3)_3N{\cdot}BH_2CO_2H$, the (protonated) boron analogue of the dipolar amino acid betaine, $(CH_3)_3N{\cdot}CH_2COO^-$.[2] A zinc complex of the amine–cyanoborane has also been reported.[4] We wish to disclose the synthesis, characterization, and preliminary investigations of the chemistry of a new class of compounds whose members are closely related to $(CH_3)_3N{\cdot}BH_2CN$. This new class of compounds may be represented as $(CH_3)_3N{\cdot}BH_2CRR'CN$ and referred to as amine–(α-cyanoorgano)boranes.

Experimental Section

Preparation of $(CH_3)_3N{\cdot}BH_2CHC_6H_5CN$ and $(CH_3)_3N{\cdot}BH_2C(CH_3)_2CN$. The procedure used is essentially the same for both compounds. The preparation of $(CH_3)_3N{\cdot}BH_2CHC_6H_5CN$ will be described with differences in the two preparations pointed out. All procedures were carried out under N_2 and all solvents transferred by using inert-atmosphere techniques. All glassware was dried overnight in an oven. The initial procedure is identical with that used by Peters for the preparation of lithium (α-cyanoorgano)trihydroborates.[5] Tetrahydrofuran was dried by distillation from $LiAlH_4$ and sodium and stored over 4A molecular sieves. A 60-mL sample of THF was syringed into flask A (held at −78 °C) followed by 10 mL of 10.1 M *n*-BuLi. The nitrile, $C_6H_5CH_2CN$ (0.025 L, 0.32 mol), was added and the solution stirred for 1 h. THF (50 mL) was then syringed into flask B (−78 °C), followed by $BH_3{\cdot}THF$ (0.05 L, 1.0 M). The contents of flask A were transferred to flask B via a double-ended needle by using positive N_2 pressure. The light yellow solution that resulted was stirred for 0.5 h. At this point this procedure differed from that utilized by Peters[5] since $LiBH_3CH(C_6H_5)CN$ was not isolated. Instead, a solution of $(CH_3)_3N{\cdot}HCl$ (14.3 g, 0.15 mol) in THF (175 mL) was gradually syringed into flask B. The resulting mixture was removed from the −78 °C slush bath and allowed to warm to ambient temperature, with N_2 flowing over the solution. The solution was stirred at ambient temperature for 22 h (16 h for the dimethyl derivative) and filtered to remove LiCl; the filtrate was then concentrated by rotary evaporation to give an oily white material. (When pure $LiBH_3CPhHCN$ is allowed to react with $(CH_3)_3N{\cdot}HCl$, a solid is obtained directly upon removal of solvent.[5]) With the phenyl derivative, this oily material was washed with diethyl ether (3 × 50 mL), and the resulting white powder was sublimed at 70 °C to give pure product (8.0 g, 85%). With the dimethyl derivative, water (100 mL) was added to the oil, followed by diethyl ether (150 mL). The organic layer was then separated from the aqueous layer and dried over $MgSO_4$, diethyl ether removed by rotary evaporation, and the resulting light yellow oil washed with hexane (3 × 50 mL) to give an oil product (6.2 g, 87%). An oil is also obtained if the intermediate lithium salt is isolated and then allowed to react with $(CH_3)_3N{\cdot}HCl$. However, crystals were obtained by washing the oil with hexane and allowing the oil–hexane mixture to stand overnight at 18 °C. These crystals may be washed with cold hexane.

Data for $(CH_3)_3NBH_2CH(C_6H_5)CN$: mp 133–134 °C dec; IR (KBr disk) 3037, 3018, 2994, 2938 (CH), 2348 (BH), 2208 ($C{\equiv}N$), 1595, 1485 (Ph, $C{=}C$), 1412, 1402 ($C{-}C{\equiv}N$), 1245 ($C{-}N$), 1156 cm^{-1} (BN); ^1H NMR ($CDCl_3$) δ 2.63 (s, 9 H, $(CH_3)_3N$), 3.12 (br, s, 1 H, CH), 7.26 (m, 5 H, C_6H_5); ^{11}B NMR ($CDCl_3$) δ −2.23 (t, BH_2, J_{B-H} = 105 Hz). Anal. Calcd for $C_{11}H_{17}BN_2$: C, 70.25; H, 9.11; N, 14.90. Found: C, 70.04; H, 9.25; N, 15.03. The solid is soluble in dichloromethane and tetrahydrofuran and insoluble in hexane, diethyl ether, and water. Data for $(CH_3)_3NBH_2C(CH_3)_2CN$: mp (crystals) 34–35 °C; IR (neat) 3020, 3010, 2960 (CH), 2385 (BH), 2210 ($C{\equiv}N$), 1408 ($C{-}C{\equiv}N$), 1245 ($C{-}N$), 1160 cm^{-1} (BN); ^1H NMR ($CDCl_3$, $(CH_3)_4Si$) δ 1.21 (s, 6 H, $C(CH_3)_2$), 2.72 (s, 9 H, $(CH_3)_3N$); ^{11}B NMR ($CDCl_3$) δ −0.17 (t, BH_2, J_{B-H} = 105 Hz). Anal. Calcd for $C_7H_{17}BN_2$: C, 60.05; H, 12.24; N, 20.01. Found (oil product): C, 59.87; H, 12.15; N, 20.20. Found (crystalline product): C, 60.43; H, 11.84; N, 19.97; B, 7.88. The product is soluble in dichloromethane, tetrahydrofuran, and diethyl ether and insoluble in hexane and water.

Results and Discussion

The synthesis of the first two members of this new class of compounds, $(CH_3)_3N{\cdot}BH_2CH(C_6H_5)CN$ and $(CH_3)_3N{\cdot}BH_2C(CH_3)_2CN$, has been accomplished by utilizing the method given in eq 1. The reaction of $Li^+BH_3CRR'CN^-$ (generated in situ)

$$Li^+BH_3CRR'CN^- + (CH_3)_3N{\cdot}HCl \xrightarrow[25\ ^\circ C]{THF} (CH_3)_3N{\cdot}BH_2CRR'CN + H_2 + LiCl \quad (1)$$

and trimethylamine hydrochloride in tetrahydrofuran at room temperature yields the amine–(α-cyanoorgano)boranes (85% yield). (The precursor $Li^+BH_3CRR'CN^-$ salts have been isolated and characterized in our laboratory.[5]) The new compounds were characterized by infrared, proton NMR, and boron-11 NMR spectroscopies and elemental analysis.

The reaction (eq 1) used to synthesize the amine–(α-cyanoorgano)boranes in an 85% yield requires a maximum reaction period of 12 h. In contrast, the reaction used to synthesize $(CH_3)_3N{\cdot}BH_2CN$ from $NaBH_3CN$ and $(CH_3)_3N{\cdot}HCl$ requires refluxing in THF for 58 h to achieve a comparable yield.[1] This result indicates that the (α-cyanoorgano)trihydroborates, $BH_3CH(C_6H_5)CN^-$ and $BH_3C(CH_3)_2CN^-$, are much more reactive species with trimethylamine hydrochloride than is cyanotrihydroborate, BH_3CN^-. This increased reactivity is due to the presence of the CRR′ group between the BH_3 and CN groups, which has the effect of reducing the capacity of the nitrile group to withdraw electron density from the BH_3 moiety. Consequently, the B–H hydrogens in the (α-cyanoorgano)trihydroborates are more reactive than those in cyanotrihydroborate. These effects on hydride activity are consistent with the fact that trialkylhydroborates (R_3BH^-)[6] are exceptionally strong reducing agents

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compared to the very mild cyanotrihydroborate anion (BH_3CN^-)[7].

The reactivity of the amine–(α-cyanoorgano)boranes also differs from that of amine–cyanoborane. For instance, the reaction of trimethylamine–cyanoborane, $(CH_3)_3N{\cdot}BH_2CN$, with 2 equiv of Meerwein's reagent in refluxing CH_2Cl_2 gives the intermediate product $(CH_3)_3N{\cdot}BH_2CN^+C_2H_5BF_4^-$, which, upon hydrolysis, is known to yield the protonated boron analgoue of betaine, $(CH_3)_3N{\cdot}BH_2COOH$.[3] Numerous attempts to extend this synthesis to the amine–(α-cyanoorgano)borane system were unsuccessful. In all cases, the product isolated did not contain the BH_2^- group, as monitored by ^{11}B NMR and infrared spectroscopies. Very mild conditions (room temperature) did not result in a reaction. The observed decomposition of the amine–(α-cyanoorgano)boranes under conditions successful for the synthesis of $(CH_3)_3N{\cdot}BH_2COOH$ from the amine–cyanoborane must result from the presence of the CRR′ moiety in the former. Thus, insertion of CRR′ changes the reactivity of the CN and/or the B–H moieties. Research is under way to further study the preparation, stability, and reactivity of amine–(α-cyanoorgano)boranes in selected chemical systems, to compare their reactivity to that of their carbon analogues, and to evaluate the biological activity of this new class of compounds.

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Synthesis and X-ray Structure of $Na_{10}[Pt_2(\mu\text{-}PO_4)_4(C_5H_3N_5O)_2]{\cdot}22H_2O$, a Complex with Doubly Deprotonated Guanine Anions Coordinated to Diplatinum(III)

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Although there have been many structural studies of complexes that have 9-substituted guanine derivatives coordinated to a transition metal, there have been very few structures solved where guanine itself is complexed to these metal ions.[2] No structural data have been reported for guanine bonded to platinum, and in the two published structures of transition-metal complexes, namely $ZnCl_3(guH_2)$ and $CuCl_3(guH_2){\cdot}2H_2O$ (guanine = guH), the guanine is protonated as the guaninium cation guH_2^+.[3]

We have found that guanine will replace the axial water ligands in $Na_2[Pt_2(\mu\text{-}PO_4H)_4(H_2O)_2]$ to give the product complex $Na_2[Pt_2(\mu\text{-}PO_4H)_4(guH)_2]$ with the guanine ligands coordinated to the axial positions.[4] This complex is soluble in aqueous sodium hydroxide, and crystals of the compound can be grown by slow evaporation of water with this solution. The crystals have the composition $Na_{10}[Pt_2(\mu\text{-}PO_4)_4(C_5H_3N_5O)_2]$, where $C_5H_3N_5O$ is the dianion derived from guanine. This structure is significant because it is the first structural example of a complexed guanine dianion, because it is the first diplatinum(III) structure with a fully deprotonated phosphate bridge, because the lattice contains a rather unusual decanegative anion, and because the thermal parameters obtained for the crystal are very small, which leads to a very precise structure determination of the anion in the molecule.

Table I. Crystallographic Data for $Na_{10}[Pt_2(\mu\text{-}PO_4)_4(C_5H_3N_5O)_2]{\cdot}22H_2O$

formula	$Pt_2P_4Na_{10}C_{50}H_{50}N_{10}O_{40}$
fw	1694.5
space group	$P\bar{1}$
a, Å	9.4077 (5)
b, Å	10.9588 (5)
c, Å	12.2968 (16)
α, deg	72.746 (11)
β, deg	86.223 (8)
γ, deg	88.095 (8)
Z	1
V, Å^3	1208.0 (3)
d_{calcd}, g/cm^3	2.329
λ, Å (graphite monochromated)	0.71073
μ(Mo Kα) cm^{-1}	61.79
T, °C	17
data collecn instrument	Enraf-Nonius CAD 4
radiation	Mo Kα
scan method	ω–2θ
data collecn range, deg	1–28, θ
no. of unique data	5824
no. of data with $F_o^2 \geq 3\sigma(F_o^2)$	5403
no. of parameters refined	420
extinction coeff	3.7 (1) × 10^{-7}
R^a	0.019
R_w^b	0.025

$^a R = \sum||F_o| - |F_c||/|\sum F_o|$. $^b R_w = [\sum w(|F_o| - |F_c|)^2/\sum W|F_o|^2]^{1/2}$.

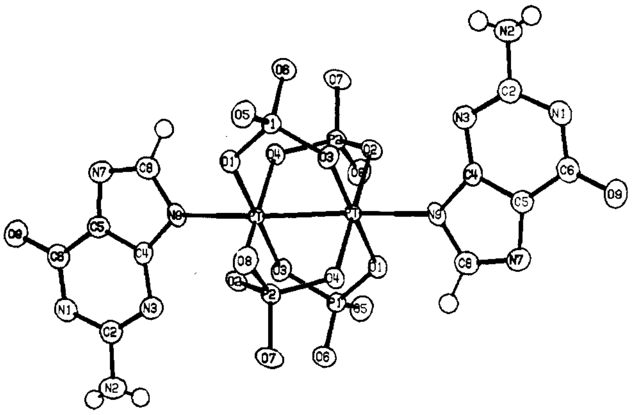

Figure 1. ORTEP view of the anion $Pt_2(\mu\text{-}PO_4)_4(C_5H_3N_5O)_2^{10-}$ with 75% probability ellipsoids.

Experimental Section

Potassium tetrachloroplatinate(II) was purchased from Matthey Bishop Inc. The complex $Na_2[Pt_2(\mu\text{-}PO_4H)_4(H_2O)_2]$ was prepared by the literature procedure.[5] Guanine was purchased from Sigma Co. The complex $Na_{10}[Pt_2(\mu\text{-}PO_4)_4(C_5H_3N_5O)_2]$ ($C_5H_3N_5O$ = doubly deprotonated guanine dianion) was prepared by the addition of guanine hydrochloride to a solution of $Na_2[Pt_2(\mu\text{-}PO_4H)_4(H_2O)_2]$ in aqueous sodium hydroxide.[4] Slow evaporation of the solvent gave the crystals as yellow rhombohedra.

Structure Solution. A yellow rhombic crystal of dimensions 0.20 × 0.32 × 0.40 mm was sealed in a capillary tube. Intensity data were obtained on an Enraf-Nonius CAD4 diffractometer equipped with Mo Kα radiation and a graphite monochromator by ω–2θ scans designed to yield $\sigma(I) = 0.04I$ for all observable data, subject to a maximum scan time of 60 s. The scan rates were 1.0–4.0°/min. One hemisphere of data was collected ($-12 \leq h \leq 12$, $0 \leq k \leq 14$, $-16 \leq l \leq 16$) and corrected for Lp, background, and absorption effects. The absorption correction was made by using ψ scans, and the minimum relative transmission

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