Table I. Analytical Results for the Complexes of the Type $[Cr(OA)_2(en)_2]^+$

OA^{-a}		% Cr	% C	% N	% H	% Cl	proposed formula
OPr^-	found	13.62	39.79	14.52	7.91		$[Cr(OPr)_2(en)_2](OPr)$
	calcd[b]	13.28	39.89	14.31	7.98		
$OiBu^-$	found	10.76	42.56	13.64	8.61		$[Cr(OiBu)_2(en)_2](OiBu)\cdot H_2O$
	calcd[b]	11.52	42.56	12.41	8.71		
$OPiv^-$	found	12.77	40.92	13.70	8.26	8.64	$[Cr(OPiv)_2(en)_2]Cl$
	calcd[b]	12.69	41.02	13.67	8.36	8.65	
OBz^-	found	9.75	55.18	10.89	6.03		$[Cr(OBz)_2(en)_2](OBz)$
	calcd[b]	9.71	56.07	10.46	5.83		
$ONic^-$	found	9.46	47.12	18.20	5.46		$[Cr(ONic)_2(en)_2](ONic)\cdot H_2O$
	calcd[b]	9.34	47.48	17.62	5.43		

[a] OPr^- = propionate, $OiBu^-$ = isobutyrate, OPiv = pivalate (2,2-dimethylpropionate), OBz^- = benzoate, $ONic^-$ = nicotinate-*O*.

Table II. UV-Visible Spectra and Molar Conductances of Complexes of the Type $[Cr(OA)_2(en)_2]^+$ in Water at 25 °C

	λ, nm (ε, L mol⁻¹ cm⁻¹)							
OA^-	λ_{max}	λ_{min}	λ_{max}	λ_{min}	λ_{max}	10*Dq*, $cm^{-1} \times 10^3$	Λ_M, S $cm^2\ mol^{-1}$	ref
OAc^{-a} (cis)			373 (44)[b]	422 (8)[b]	503 (83)[b]	19.9		6
OAc^- (trans)			373 (46)[b]	465 (18)[b] 420 sh (25)[b]	530 (40)[b]	18.9		6
OPr^-			372 (61.8)	422 (17.9)	497 (110)	20.1	65.3	this work
$OiBu^-$			372 (59.6)	422 (19.0)	497 (99.4)	20.1	131	this work
$OPiv^-$			372 (61.6)	423 (18.4)	498 (106)	20.1	96.6	this work
OBz^-	231 (35 000)	308 (43.3)	355 (68.6)	423 (29.1) 460 sh (40)	498 (55.3)	20.1	60.2	this work
$ONic^-$ (cis)	261 (11 500)	331 (29.3)	370 (67.1)	418 (24.5)	490 (107)	20.4		7
$ONic^-$	262 (11 200)	315 (131)	342 (141)	430 (46.9) 470 sh (50)	493 (57.0)	20.3	93.5	this work

[a] OAc = acetate. [b] Estimated from the spectral curves in the cited literature.

the spectra of the propionate, isobutyrate, and pivalate complexes all resemble the spectrum of *cis*-$[Cr(OAc)_2(en)_2]^+$, suggesting the cis configuration for these complexes. This is in contrast to the finding of Vaughn et al.[1] for the configuration of the bis(acetato)bis(1,3-propanediamine)chromium(III). The spectra of the benzoate and the nicotinate complexes exhibit a slight shoulder at 460-470 nm, suggesting the trans configuration for these two complexes. The spectrum of the nicotinate complex reported here is different from that of *cis*-$[Cr(ONic)_2(en)_2]^+$ reported earlier.[7] Actually, the spectrum of *cis*-$[Cr(ONic)_2(en)_2]^+$ is very similar to the spectra of the aliphatic carboxylate complexes; this spectrum is also included in Table II for comparison.

In order to ascertain the lability of these complexes qualitatively, the visible spectra of the aqueous solutions of these complexes were scanned over a period of 30 min at ca. 25 °C. For the three aliphatic carboxylate complexes the λ_{max} were shifted to longer wavelengths slowly and three isosbestic points were observed as follows: OPr^- 545, 435, 396 nm; $OiBu^-$ 548, 436, 400 nm; $OPiv^-$ 553, 434, 403 nm. The percentage decrease in the absorbance at the low-energy maximum, over a period of 20 min, was ca. 21%, 15%, and 12% for the propionate, isobutyrate, and pivalate complexes, respectively, suggesting that the most branched aliphatic carboxylate ligand (pivalate) reacts the slowest.

The visible spectra of the benzoate and the nicotinate complexes changed very little over a 60-min period. For the nicotinate complex, the absorbance at 495 nm showed less than 3% decrease in 2.5 h and ca. 17% decrease after 24 h.

In 0.1 M $HClO_4$ solutions, these complexes showed much faster decrease in the absorbances and shifts of λ_{max} to longer wavelengths. For the three aliphatic carboxylate complexes, only one isosbestic point at ca. 527 nm was observed. Two more isosbestic points were near λ_{min} and could not be accurately determined. For the benzoate complex, also only one isosbestic point at 522 nm was observed while the other two near λ_{min} could not be determined. The differences in the isosbestic points in aqueous solutions and in $HClO_4$ solutions suggested different reaction paths in water and in acid. This is not surprising because of the tendency of both the carboxylate and the diamine to protonate in acidic solutions. Also, the Cr-N rupture path was observed in other Cr(III)-amine complexes.[9-13] More detailed studies of the reactions of these complexes are under way.

The visible spectrum of the nicotinate complex in 0.1 M $HClO_4$ also changed very little with time. The absorbance at 342 nm showed only a 7% decrease over a 24-h period at ca. 25 °C. the biological activity of this complex has not been tested.

Registry No. $[Cr(OPr)_2(en)_2](OPr)$, 101652-58-8; $[Cr(OiBu)_2(en)_2](OiBu)$, 101652-60-2; $[Cr(OPiv)_2(en)_2](OPiv)$, 101670-92-2; $[Cr(OBz)_2(en)_2](OBz)$, 101652-62-4; $[Cr(ONic)_2(en)_2](ONic)$, 101758-89-8.

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The Unusual Structural Feature of Binuclear Platinum Chains $[Pt_2(L\text{-}L)_4X]^{n-}_{\infty}$

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Binuclear platinum chains $[Pt_2(L\text{-}L)_4X]^{n-}_{\infty}$, **1** (L-L = $CH_3CS_2^-$, X = I, $n = 0$; L-L = $(HO_2P\text{-}O\text{-}PO_2H)^{2-}$, X = Br, $n = 4$),[1] contain platinum atoms of formal oxidation state +2.5 and have a symmetrical $Pt^{2.5+}\text{-}X\text{-}Pt^{2.5+}$ bridge.[2] These binuclear chains are closely related to mixed-valence, mononuclear platinum analogues

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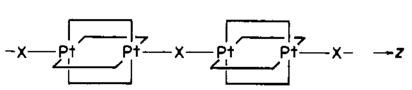

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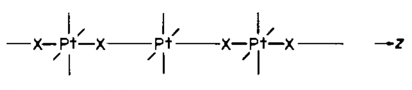
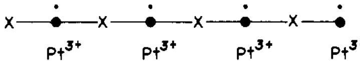
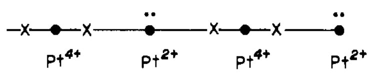


$[Pt^{4+}L_4X_2{\cdot}Pt^{2+}L_4]_\infty$, **2**.[3,4] It is well-known that mononuclear chains **2** do not adopt a symmetrical Pt^{3+}–X–Pt^{3+} bridge (**3a**) but an asymmetrical Pt^{4+}–X···Pt^{2+} bridge (**3b**).[3-5] The d_{z^2} band of **3a** is half-filled since each Pt^{3+} site contributes one electron to the band. Thus the pairing-distortion of bridging halides, **3a** → **3b**, is a consequence of the Peierls instability associated with a half-filled band.[5,6] Each binuclear $Pt_2(L\text{-}L)_4$ unit has two d_{z^2} orbitals so that **1** consists of two d_{z^2} bands, one largely derived from the bonding combination and the other from the antibonding combination of two d_{z^2} orbitals in each $Pt_2(L\text{-}L)_4$ unit. Since each $Pt_2(L\text{-}L)_4$ unit contributes three electrons to the two d_{z^2} bands, the higher lying one becomes half-filled. By analogy with mononuclear platinum chains **2**, it is expected that binuclear platinum chains **1** would also undergo a Peierls distortion **4a** → **4b** (i.e., a dimerization that doubles the unit cell size) and thus have an asymmetrical Pt^{3+}–X···Pt^{2+} bridge. Apparently this is not observed in binuclear platinum chains, **1**.[1,2]

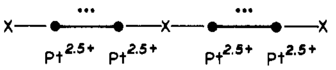
3a



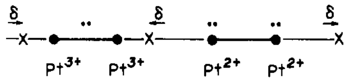
3b



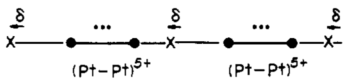
4a



4b



4c



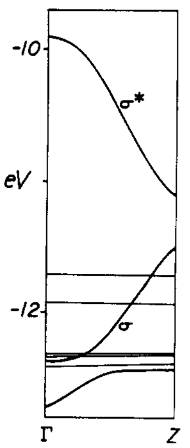


Figure 1. Dispersion relationships of the occupied d-block bands calculated for the $[Pt_2(HCS_2)_4I]$ chain, **4a**. The dispersive bands σ and σ* are largely based upon the d_{z^2} orbitals, and the σ* band is half-filled. The wavevectors Γ and Z are defined as follows: Γ = 0 and Z = π/d, where d is the repeat distance of the chain **4a**.

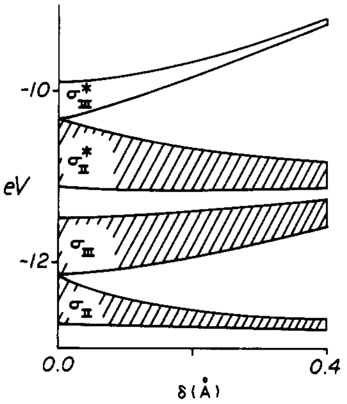


Figure 2. Widths of the d_{z^2} bands of a binuclear platinum chain $[Pt_2(HCS_2)_4I]_\infty$ as a function of the pairing distortion of bridging halides, **4a** → **4b**. The shaded area indicates that each band orbital is doubly occupied, which is valid under the assumption that **4a** and **4b** adopt low-spin states.

According to a preliminary report of Butler et al.,[7] a low-temperature (19 K) crystal structure of $[Pt_2(HO_2P\text{–}O\text{–}PO_2H)_4Br]^{4-}{}_\infty$ chain is consistent with structure **4c**, which has unequal Pt–Br distances of 2.579 and 2.778 Å. The structural change **4a** → **4c** is not a Peierls distortion, so that it is difficult to rationalize why this distortion is energetically favored. Despite the presence of symmetrical $Pt^{2.5+}$–X–$Pt^{2.5+}$ bridges, however, the binuclear platinum chain compounds are all reported to be semiconducting, not metallic.[1] To gain some insight into the origin of these apparently puzzling properties, we examined the **4a** → **4b** and **4a** → **4c** distortions of a model chain $[Pt_2(HCS_2)_4X]$ (X = I) as a function of the halide ion displacement δ by performing tight-binding band calculations,[8] based upon the extended Hückel method.[9,10]

Results and Discussion

Figure 1 shows the occupied d-block bands of **4a** (X = I), where the dispersive bands σ and σ* are largely made up of bonding combination ϕ_+ and antibonding combination ϕ_- of two d_{z^2} orbitals in each dimeric unit $Pt_2(HCS)_4I$, respectively. In the region of

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(2) In the case of $[Pt_2(CH_3CS_2)_4I]_\infty$, the Pt–X–Pt bridge is not exactly but nearly symmetrical (i.e., Pt–I = 2.975, 2.981 Å).[1a] Nevertheless, we employ the phrase "a symmetrical Pt–X–Pt bridge" for this case as well to emphasize its striking difference from a strongly asymmetrical Pt–X···Pt bridge present in mixed-valence chains (e.g., Pt–I = 2.791, 3.036 Å in $[Pt(NH_2CH_2CH_2NH_2)_2Pt(NH_2C_2CH_2NH_2)_2I_2]^{4+}$).[3d]

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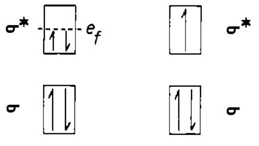
(10) The atomic parameters employed in the present calculations were taken from ref 5a.

the σ bond, there occur a number of flat bands (i.e., six bands of mainly d_{xz}, d_{yz}, and d_{xy} orbitals, two bands of mainly bridging iodide x and y orbitals, and one band of mainly sulfur x and y orbitals). With $Pt_2(HCS_2)_4X$ as a unit cell, all the bands of Figure 1 up to σ are completely filled, while one electron per unit cell is left over to fill the σ^* band. Since the flat bands of either metal or ligand in origin are not significantly affected by the distortions **4a** → **4b** and **4a** → **4c**, we will examine only the σ and σ^* bands for simplicity.

The uniform chain **4a** may adopt a low-spin metallic state **5a**. Figure 2 shows how the σ and σ^* bands of **4a** split as δ increases during the **4a** → **4b** distortion. The major components of the σ_{II} and σ_{III} bands are ϕ_+ orbitals of $(Pt^{2+})_2(L\text{-}L)_4$ and $(Pt^{3+})_2(L\text{-}L)_4$ units, respectively. Likewise, the main orbital components of $\sigma_{II}{}^*$ and $\sigma_{III}{}^*$ bands are the ϕ_- orbitals of $(Pt^{2+})_2(L\text{-}L)_4$ and $(Pt^{3+})_2(L\text{-}L)_4$ units, respectively. The orbitals of bridging halides have antibonding interactions with the ϕ_+ and ϕ_- orbitals of $Pt_2(L\text{-}L)_4$ units. Thus the σ_{III} and $\sigma_{III}{}^*$ bands lie higher in energy than the σ_{II} and $\sigma_{II}{}^*$ bands, respectively.



5a 5b

Our calculations show **4b** to have the energy minimum at $\delta_{min} \simeq 0.16$ Å with the band gap of 0.70 eV, which is more stable than **4a** by 1 kcal/mol per $Pt_2(HCS_2)_4I$. The **4a** → **4c** distortion does not open a band gap at the Fermi level of **5a**. Calculations were also performed for this distortion to simulate the low-temperature structure of $[Pt_2(HO_2P\text{-}O\text{-}PO_2H)_4Br]^{4-}{}_\infty$ chain proposed by Butler et al.,[7] which show that the stability of the chain decreases with increasing δ. All of these calculated results, though apparently in disagreement with available experimental evidence, are expected ones based upon the concept of Peierls distortion. Nevertheless, the magnitude of stabilization, ΔE, calculated for the Peierls distortion **4a** → **4b** is considerably smaller than that for the corresponding distortion **3a** → **3b** (e.g., $\Delta E \sim 40$ kcal/mol per $Pt^{4+}L_4X_2{\cdot}Pt^{2+}L_4$, where L = NH_3 and X = Cl).[5a]

Upon the **3a** → **3b** distortion, two electrons in the antibonding orbital of each $Pt^{3+}\text{-}X\text{-}Pt^{3+}$ bridge in **3a** become a nonbonding electron pair of a Pt^{2+} site in **3b** so that the ΔE term is substantial.[5] In **4b**, there occurs two-orbital four-electron destabilization[11] in each $(Pt^{2+})_2(L\text{-}L)_4$ moiety. In addition, two electrons in each $(Pt^{3+})_2(L\text{-}L)_4X_2$ unit experience enhanced antibonding between bridging halides and Pt^{3+} sites. Furthermore, in each $(Pt^{2+})_2(L\text{-}L)_4$ unit of **4b**, there occurs intersite Coulomb repulsion between the Pt^{2+} sites. Consequently, the tendency for Peierls distortion is weaker for the binuclear platinum chains than for the mononuclear platinum chains.

So far our discussion of the **4a** → **4b** and **4a** → **4c** distortions is based upon the assumption that there is no electron localization (i.e., there is no unpaired electron) in the regular structure **4a**. This assumption leads to a couple of problems difficult to explain. (a) Each $[Pt_2(L\text{-}L)_4X]^{n-}{}_\infty$ chain does not undergo a Peierls distortion despite its half-filled band, and (b) the binuclear platinum compounds are not metallic despite the absence of a Peierls distortion in each $[Pt_2(L\text{-}L)_4X]^{n-}{}_\infty$ chain. An alternative electronic state of **4a** that avoids the above problems is the localized state **5b**, which represents all situations where an electron is localized in every $Pt_2(L\text{-}L)_4$ unit.[5b] Bellitto et al.[1a] observed the diffuse-reflectance spectrum of $Pt_2(CH_3CS_2)_4I$ to have a strong broad peak centered at about 1.3 eV, which is assigned to transitions between σ and σ^* bands. The electrical conductivity data on $Pt_2(CH_3CS_2)_4I$ showed a thermal activation energy E_a of 0.05–0.06 eV, which is about 2 orders of magnitude smaller than the reflectance peak. Thus Bellitto et al.[1a] concluded that the electrical conduction in $Pt_2(CH_3CS_2)_4I$ is better described by a hopping mechanism rather than by a band mechanism. A hopping mechanism of electrical conduction assumes the presence of localized electrons on lattice sites and hence is consistent with the localized picture **5b** for a $[Pt_2(L\text{-}L)_4X]^{n-}{}_\infty$ chain. The presence of a strong broad peak in the reflectance spectrum of $Pt_2(CH_3CS_2)_4I$ is also consistent with the localized state **5b**, since this state allows electronic transition that begins from the top of the σ band to the bottom of the σ^* band.

Although the localized state **5b** for the chain **4a** avoids a number of conceptual problems associated with the delocalized state **5a**, we must point out a couple of questions concerning the localized state. (a) The structural distortion **4a** → **4c** proposed by Butler et al.[7] is not calculated to be favorable even under the assumption that both **4a** and **4c** adopt localized electronic states. Our calculations for this distortion, with high-spin electron configurations for **4a** and **4c**, show that the chain becomes less stable with increasing δ. (b) One might expect that the magnetic susceptibility of the binuclear platinum compound would exhibit some paramagnetic behavior due to the presence of localized electrons on each $Pt_2(L\text{-}L)_4$ site. Nevertheless, $Pt_2(CH_3CS_2)_4I$ is found to be diamagnetic.[1a] Consequently, one may have to speculate that there occurs some kind of spin-pairing phenomenon in such compounds. Recently, the binuclear nickel chain $[Ni_2(CH_3CS_2)_4I]_\infty$ was found to have the structural and electronic properties similar to those of its platinum analogue $[Pt_2(CH_3CS_2)_4I]_\infty$.[12] Our conclusions concerning the electronic structure of the latter are also applicable to the former.

Concluding Remarks

The structures of binuclear platinum chains **1** are not explained by the concept of Peierls instability, in contrast to the case of the corresponding mononuclear platinum chains **2**. The electrical properties of the binuclear platinum chains are better described by the localized electronic state **5b** than by the delocalized state **5a**. Nevertheless, unsatisfactory aspects exist in the localized picture. In view of the fact that the concept of Peierls instability has been essential in understanding the structural and electronic properties of various low-dimensional materials, binuclear platinum chains **1** deserve further experimental and theoretical studies.

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Registry No. Pt, 7440-06-4; $Pt_2(HCS_2)_4I$, 101630-47-1.

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Proposed Reformulation of the Recently Reported $TaBr_3(PMe_2Ph)_2$

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Received February 12, 1986

A recent paper in *Inorganic Chemistry* by Hovnanian et al.[1] described the synthesis and properties of a compound formulated as monomeric pentacoordinate, $TaBr_3(PMe_2Ph)_2$. The main stereochemical feature of this compound, namely square-pyramidal coordination such that the square basal plane of ligands incor-

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