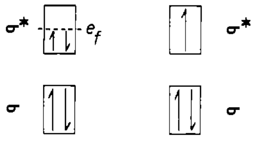
the σ bond, there occur a number of flat bands (i.e., six bands of mainly d_{xz}, d_{yz}, and d_{xy} orbitals, two bands of mainly bridging iodide x and y orbitals, and one band of mainly sulfur x and y orbitals). With $\mathrm{Pt_2(HCS_2)_4X}$ as a unit cell, all the bands of Figure 1 up to σ are completely 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 $\mathrm{(Pt^{2+})_2(L\text{-}L)_4}$ and $\mathrm{(Pt^{3+})_2(L\text{-}L)_4}$ units, respectively. Likewise, the main orbital components of σ_{II}^* and σ_{III}^* bands are the ϕ_- orbitals of $\mathrm{(Pt^{2+})_2(L\text{-}L)_4}$ and $\mathrm{(Pt^{3+})_2(L\text{-}L)_4}$ units, respectively. The orbitals of bridging halides have antibonding interactions with the ϕ_+ and ϕ_- orbitals of $\mathrm{Pt_2(L\text{-}L)_4}$ units. Thus the σ_{III} and σ_{III}^* bands lie higher in energy than the σ_{II} and σ_{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 $\mathrm{Pt_2(HCS_2)_4I}$. 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 $[\mathrm{Pt_2(HO_2P\text{-}O\text{-}PO_2H)_4Br}]^{4-}_\infty$ 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 $\mathrm{Pt^{4+}L_4X_2{\cdot}Pt^{2+}L_4}$, where L = $\mathrm{NH_3}$ and X = Cl).[5a]

Upon the **3a** → **3b** distortion, two electrons in the antibonding orbital of each $\mathrm{Pt^{3+}\text{-}X\text{-}Pt^{3+}}$ bridge in **3a** become a nonbonding electron pair of a $\mathrm{Pt^{2+}}$ site in **3b** so that the ΔE term is substantial.[5] In **4b**, there occurs two-orbital four-electron destabilization[11] in each $\mathrm{(Pt^{2+})_2(L\text{-}L)_4}$ moiety. In addition, two electrons in each $\mathrm{(Pt^{3+})_2(L\text{-}L)_4X_2}$ unit experience enhanced antibonding between bridging halides and $\mathrm{Pt^{3+}}$ sites. Furthermore, in each $\mathrm{(Pt^{2+})_2(L\text{-}L)_4}$ unit of **4b**, there occurs intersite Coulomb repulsion between the $\mathrm{Pt^{2+}}$ 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 $[\mathrm{Pt_2(L\text{-}L)_4X}]^{n-}_\infty$ 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 $[\mathrm{Pt_2(L\text{-}L)_4X}]^{n-}_\infty$ 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 $\mathrm{Pt_2(L\text{-}L)_4}$ unit.[5b] Bellitto et al.[1a] observed the diffuse-reflectance spectrum of $\mathrm{Pt_2(CH_3CS_2)_4I}$ 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 $\mathrm{Pt_2(CH_3CS_2)_4I}$ 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 $\mathrm{Pt_2(CH_3CS_2)_4I}$ 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 $[\mathrm{Pt_2(L\text{-}L)_4X}]^{n-}_\infty$ chain. The presence of a strong broad peak in the reflectance spectrum of $\mathrm{Pt_2(CH_3CS_2)_4I}$ 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 $\mathrm{Pt_2(L\text{-}L)_4}$ site. Nevertheless, $\mathrm{Pt_2(CH_3CS_2)_4I}$ 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 $[\mathrm{Ni_2(CH_3CS_2)_4I}]_\infty$ was found to have the structural and electronic properties similar to those of its platinum analogue $[\mathrm{Pt_2(CH_3CS_2)_4I}]_\infty$.[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.

Acknowledgment. This work was supported by the Camille and Henry Dreyfus Foundation through a Teacher-Scholar Award to M.-H.W. (1980–1985).

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

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Proposed Reformulation of the Recently Reported $\mathrm{TaBr_3(PMe_2Ph)_2}$

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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, $\mathrm{TaBr_3(PMe_2Ph)_2}$. The main stereochemical feature of this compound, namely square-pyramidal coordination such that the square basal plane of ligands incor-

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porates the central metal atom, is not in accordance with voluminous prior structural information on five-coordination. This together with some other unusual properties of the complex raises serious doubts as to its correct identification. The interatomic dimensions, especially bond angles, in the molecule of "$TaBr_3(PMe_2Ph)_2$" are so close to those in $TaCl_4(PMe_2Ph)_2$,[2] that it is reasonable to suspect that both of them are in fact of the same type, viz. $TaX_4(PMe_2Ph)_2$. If instead of two disordered Br atoms (17.5 electrons each) we were to use two nondisordered Cl atoms (17 electrons each) there would be no significant effect on the quality of the refinement. On the other hand it would explain the short (ca. 2.38 Å) Ta–X distance. A Ta–Br bond length of this shortness is not acceptable.

For the above reasons we believe that the compound is in fact a six-coordinate octahedral Ta(IV) complex, $TaCl_xBr_{4-x}(PMe_2Ph)_2$, with x equal to or close to 2. This change eliminates all unusual features of the molecular structure and is also consistent with the reported composition determined by elemental analysis (two Cl atoms instead of one Br diminish the molecular weight by only 9 daltons, less than 2%). The presence of chlorine atoms is readily accounted for by the nature of the reaction medium. The combination of Mg, CH_2Cl_2, and Et_2O is likely to produce a chloro Grignard compound, which can easily cause halide ion exchange.

Other reported properties of the material, especially the solution behavior, are confusing. The interpretation of spectra is somewhat ambiguous, and contradictions can be found. While we shall not offer a detailed reanalysis of the spectral data at this time, here are a few examples of some facts that should have been addressed by the authors.

(a) It is not generally easy to observe an EPR signal for a d^2 species, while it is for a d^1 species.

(b) An agostic H atom interacting with a paramagnetic center is not likely to give a detectable NMR signal.

(c) Sharp and not shifted NMR resonances are not compatible with the observed EPR activity of the compound.

In general the magnetic data (solid-state $\mu = 1.19\ \mu_B$) and both NMR and EPR spectra are consistent with a d^1, rather than a d^2, configuration of the tantalum atom. The spectra can be qualitatively explained by the monomer (paramagnetic)–dimer (diamagnetic) equilibria known to exist for some $MCl_4(PR_3)_2$ species.[3] Our work in that area has shown that the solution chemistry is really very complex. On several occasions we discussed the peculiar green solution–red solid phenomenon that is mentioned by the authors. We also found[4] that in the presence of excess phosphine Nb(III) forms an octahedral $NbBr_3(PMe_2Ph)_3$ complex, and the same can be reasonably expected for tantalum.

The reformulation of the compound as a six-coordinate Ta(IV) complex does not rule out its ability to activate a C–H bond. Octahedral Ta(IV) species readily increase coordination number to seven or eight by the formation of TaX_4L_3 or $Ta_2X_8L_4$. Thus the major feature responsible for the postulated activity, namely availability of an unoccupied coordination site, is not lost even with six ligands around Ta. Clearly, however, more evidence is required to clarify this and other phenomena connected with this compound.

In conclusion, both the results presented in the paper itself and earlier studies[2-4] on related species strongly favor the $TaCl_2Br_2L_2$ alternative over the proposed unusual $TaBr_3L_2$ one.

Acknowledgment. We thank the Robert A. Welch Foundation (Grant No. A-494) for support of our work on the chemistry of niobium and tantalum.

Registry No. $TaBr_3(PMe_2Ph)_2$, 99211-55-9; $TaCl_2Br_2(PMe_2P)_2$, 101566-49-8.

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Hexaaza Macrocyclic Complexes of the Lanthanides

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Received February 25, 1985

The complexes of the lanthanide(III) ions with unidentate as well as bidentate chelating ligands are known to be extremely labile, their complexation and ligand-exchange equilibria being usually attained almost instantaneously.[1] Thus even very stable complexes of bidentate chelating ligands—e.g. tris(acetylacetonato)lanthanum(III) with $\beta_3 = 14.5$[2] or tris(2-pyridinecarboxylato)lanthanum(III) with $\beta_3 = 10.0$[3] —exist in aqueous solution as a mixture of species, of which the uncomplexed (hydrated) metal ion is an appreciable component. Lanthanide complexes of fused polychelated noncyclic ligands still give relatively fast reactions, but those of cyclic ligands may display considerable inertness: with ethylenediaminetetraacetate (β = 14–18 depending on metal radius[4]) metal exchange is complete within a fraction of a second;[5] complexation of Eu(III) with the tetracarboxylate derived from cyclam ($DOTA^{4-}$, $\beta = 28$) is instead very slow.[6]

The time frame of metal-exchange and ligand-exchange kinetics becomes a major consideration when lanthanide complexes are to be used as probes for biological systems. In the dilute aqueous or aqueous–organic solutions required for these systems, which often involve potentially competing ligands, even a highly stable complex, if labile, may not give reliable results. For this reason, the report by Hart and co-workers[7] that La(III) and Ce(III) are capable of forming macrocyclic complexes of the type $[M(C_{22}H_{26}N_6)]^{3+}$ and that these do not undergo metal exchange in solution appeared to be exceptionally interesting. Although these authors reported failure to extend the macrocyclic synthesis to the other members of the lanthanide series, we felt that the unique inertness of such compounds—if indeed they could be obtained—would open new possibilities in the field of lanthanide chemistry and thus warranted further study. We therefore set out to systematically investigate the conditions leading to the metal-templated macrocyclic synthesis and have now successfully obtained, by an appropriate combination of counterions and experimental conditions, two series of complexes of the macrocyclic ligand $L = C_{22}H_{26}N_6$, with every lanthanide(III) ion except radioactive Pm. We describe here their synthesis, characterization, and properties. As our work was nearly completed, a parallel study of lanthanide macrocycles was reported by Fenton and co-workers;[8] their systems differ from ours in having peripheral H atoms instead of $-CH_3$ groups and include cycles with $-CH_2CH(CH_3)-$ and $-(CH_2)_3-$ side chains.

Experimental Section

Template Synthesis of the $LnL(OH)(ClO_4)_2 \cdot mH_2O$ Complexes (Ln = La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Ho, Er, Yb; m = 0–2). A mixture of lanthanide perchlorate (1.0 mmol in 20 mL of methanol, stored for several days over Linde 4A molecular sieves), 2,6-diacetylpyridine (2.0 mmol in 20 mL of methanol), and 1,2-diaminoethane (2.0 mmol, 5.0 mL

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