are reacted with 1 equiv of $[(C_5H_5)_2Fe]BF_4$, the oxidized products precipitate from the reaction mixture leaving the other products $[(C_5H_5)_2Fe$ and $(Ph_4P)BF_4]$ in solution. Pentane extraction of the precipitate gives $[(O)M(S\text{-}2,4,6\text{-}i\text{-}Pr_3C_6H)_4]$ (Mo (**5**), W (**6**)) as microcrystals in 50–65% yields.[10] Electrochemical and electronic spectroscopic studies of the chemically oxidized compounds demonstrates that **5** and **6** are identical with the species produced by the electrochemical oxidations. The complexes dissolve in toluene and alkanes to give intense blue solutions. These solutions are stable for >24 h for **6** and for several hours for **5**. The crystalline solids show decomposition after several days at room temperature but they are stable at −20 °C for extended periods. The complexes react with donor solvents such as DMF as indicated by the substantial changes in the electronic spectra; again, **5** is more reactive than **6**. This reactivity trend provides a probable explanation for the electrochemical behavior in DMF solution.

The electronic spectra of **5** and **6** are characterized by intense absorptions at 803 and 644 nm, respectively. In both cases, this band is considerably shifted to lower energy in comparison to the low-energy band in the M(V) complexes; the shifts are consistent with their assignments as a S-to-metal charge-transfer transition. ^1H NMR spectroscopy demonstrates the diamagnetism of **5** and **6** and the equivalence of the four thiolate ligands; this is consistent with a square-pyramidal structure similar to that of the $[(O)M^V(SR)_4]^-$ complexes and to the structure of $[(O)Mo(OC_4F_9)_4]$.[11] This work serves as another example of the ability of sterically hindered thiolate ligands to stabilize metal–thiolate coordination for metals in high oxidation states.[8,12]

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Supplementary Material Available: Structural diagrams and tables of crystallographic information, fractional coordinates, bond distances and angles, and thermal parameters for **1** and **2** (8 pages). Ordering information is given on any current masthead page.

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(10) $[(O)Mo(S\text{-}2,4,6\text{-}i\text{-}Pr_3C_6H_2)_4]$: electronic spectrum (pentane) 803 nm ($\epsilon = 8900$); IR (Nujol) 940 cm^{-1}, ν(Mo–O); ^1H NMR (C_6D_6) δ 1.203 (12 H, d), 1.208 (6 H, d), 2.782 (2 H, m), 3.549 (1 H, m), 7.058 (2 H, s). $[(O)W(S\text{-}2,4,6\text{-}i\text{-}Pr_3C_6H_2)_4]$: 750 (sh) ($\epsilon = 5100$), 643 ($\epsilon = 9390$), 480 ($\epsilon = 1490$), 420 nm ($\epsilon = 1080$); 959 cm^{-1}, ν(W–O); δ 1.204 (12 H, d), 1.210 (6 H, d), 2.815 (2 H, m), 3.548 (1 H, m), 7.057 (2 H, s).

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Dichlorotetrakis(pyridine)cobalt(III): A Versatile and Facile Synthetic Precursor

Sir:

The *trans*-dichlorotetrakis(pyridine)cobalt(III) complex, $Co(py)_4Cl_2^+$, was first synthesized by Werner and Feenstra in 1906.[1] It was employed in the 1950s to aid in the elucidation of the S_N1cb mechanism.[2] Nevertheless, despite its long history, only a few research groups seem to be aware of the synthetic utility of the complex as a facile route to chelated complexes. In this paper, we note several applications of the complex to Co(III) synthesis, some advantages over other synthetic precursors, and some preliminary investigations into the mechanism(s) leading to complex formation.

Table I. Distribution of $Co(dien)_2^{3+}$ Geometric Isomers

isomer	proportion, %[a]	equilibrium proportion, %[b]
s-fac	1.3	7
u-fac	7.0	29
mer	91.7	64

[a] $Co(py)_4Cl_2^+$ precursor; this work. [b] Reference 16 (counterion = NO_3^-).

Chan and Hui used the title complex in the slurry synthesis of pentakis(alkylamine)chlorocobalt(III) complex.[3] However, Toftlund and Pedersen seem to be one of the first groups to employ the compound in a facile solution synthesis of chelated CoN_6^{3+} complexes.[4] Their syntheses, performed in 2-methoxyethanol solvent systems, utilized near-stoichiometric amounts of ligands (both *cis*- and *trans*-1,2-cyclopentanediamine) and produced yields as high as 82%.[4]

In the last 10 years,, a few other groups have utilized $Co(py)_4Cl_2^+$ to synthesize other tris(diamine), polyamine, and mixed multidentate amine–thioether complex.[5–11] Many of these syntheses involved the use of stoichiometric amounts of ligands and organic solvents such as methanol, ethanol, pyridine, and dimethyl sulfoxide. Most of these reports refer to an almost instantaneous reaction, which seems odd given the slow rate of aquation of this complex.[2,12] We, therefore, have examined in more detail the parameters affecting the complex formation reactions of this complex and the product distributions resulting from reactions of the title complex with multidentate ligands.

When an aqueous solution of *trans*-$[Co(py)_4Cl_2]NO_3$ is mixed with a solution containing an excess of tetrasodium ethylenediaminetetraacetate, Na_4EDTA, the pale green solution rapidly changes color to blue-green. The visible spectrum of the resulting solution identifies the product as $[Co(EDTA)Cl]^{2-}$ with peak maxima at 584 and 404 nm (lit.[13] 584 and 402 nm). The solution then slowly reverts to the violet $Co(EDTA)^-$ complex. The formation of the chloro complex implicates electron transfer rather than substitution as the pathway for rapid complex formation. Trace amounts of Co(II) will complex with the $EDTA^{4-}$, followed by facile oxidation by $Co(py)_4Cl_2^+$ via an inner-sphere electron-transfer reaction. Wilkins and Yelin have reported on the kinetics of this process with the preformed Co(II)–EDTA complex.[14]

The title complex also reacts rapidly with pentaethylenehexamine, linpen, in aqueous solution. Visual observation of the green to yellow color change indicates, again, a nearly instantaneous reaction. Due to the very intense peak at 295 nm for the $Co(py)_4Cl_2^+$ complex,[15] we were able to follow this reaction in very

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dilute solution. For a solution approximately 1×10^{-5} M in $Co(py)_4Cl_2^+$ and approximately 1×10^{-4} M in linpen, the disappearance of $Co(py)_4Cl_2^+$ is first order with a half-life of 48 s. When the same concentrations are maintained and approximately 2×10^{-6} M $Co(H_2O)_6^{2+}$ is added, the half-life falls to 24 s. Thus, as with the reaction with $EDTA^{4-}$ above, electron transfer is indicated as the pathway for rapid complex formation.

The efficiency of these complex formation reactions is indicated by the following preparation. When 0.25 g of $[Co(py)_4Cl_2]NO_3$ (0.0005 mol) in 50 mL of H_2O is allowed to react with 0.20 g of diethylenetriamine, dien (0.002 mol), in 10 mL of H_2O, an immediate color change to yellow is observed. Cation exchange of the product solution on a column of SP-Sephadex by elution with 0.05 M Na_3PO_4 separates the $Co(dien)_2^{3+}$ product into its three geometric isomers.[16] The total yield of the three isomers was near 100% based upon title complex used, and no other Co(III) species were observed. Furthermore, the isomer distribution (*s-fac*:*u-fac*:*mer*) was far from the equilibrium isomer distribution as indicated in Table I. The increase in the proportion of *mer* isomer at the expense of both the *u-fac* and *s-fac* isomers is in the direction predicted by Favas and Kepert[17] if the isomer distribution were reflecting that of $Co(dien)^{2+}$ rather than the 3+ complex. Hence, the product distribution is also supportive of electron transfer as the mode of complex formation.

The title complex, then, appears to be generally applicable to a wide variety of synthetic applications. Chromophores of the CoN_6^{3+} type have received the most attention,[4-9] but mixed CoN_4S_2,[10] CoN_4SCl,[11] and CoN_2O_3Cl[18] chromophores can also form rapidly from this precursor. Nonequilibrium isomer distributions are achieved with polyamines, which could lead to unattainable products or products produced in only low yields by more conventional synthetic routes. The complex may also be utilized for mixed-ligand syntheses. We have obtained yields of 20–30% for the (cysteinato)bis(ethylenediamine)cobalt(III) complex[19] by reacting the title complex with a 10% excess of a 1:2 ligand mixture in aqueous solution.

A major advantage in the use of this complex as a synthetic precursor is the rapid complex formation achieved at ambient temperatures with stoichiometric amounts of ligands and/or dilute solutions of ligands. The complex is also soluble in a wide variety of solvents, and synthesis is possible in any of these. The original synthetic procedure of Werner and Feenstra[1] has been improved by two groups.[20,21] We observe little difference in the synthetic utility of the compound prepared by either procedure, indicating that catalytic amounts of Co(II) are present when either method is followed. The solid complex is stable for months on the shelf.[20]

The more commonly used "tris(carbonato)cobaltate(III)" complex is applicable to a wide variety of synthetic applications, but syntheses with this complex usually employ an excess of ligands, and removal of the third carbonato group is often sluggish.[22] Also, strictly nonaqueous preparations with this compound would be difficult since the complex is usually prepared just before use with aqueous hydrogen peroxide.[22]

This study has shown that the mode of rapid complex formation between this complex and ligands is undoubtedly via electron-transfer processes, and previous kinetic studies in this area indicate that the complex is a facile oxidant by either an inner-sphere[14] or an outer-sphere[15] route with many Co(II) complexes. For the inorganic chemist who wishes to employ this complex, the preliminary mechanistic studies reported here suggest two useful experimental notes. First, if a synthesis is being attempted and the reaction is sluggish, a trace of Co^{2+} should speed up the reaction as noted above. Second, if physical solution studies are being made, care should be taken in the choice of buffers employed unless the complex is completely free of Co(II).

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Electronic Control of the Structural Stability of Quasi-Periodic Linear Chains

Sir:

The recent notion of quasi-periodic systems proposed by Steinhardt and colleagues coupled with the observed icosahedral symmetry of electron diffraction patterns in Mn–Al alloys presents systems conceptually intermediate between a random network and the crystalline solid.[1,2] The pentagonal symmetry properties are incommensurate with translational symmetry yet represent a nonrandom arrangement of atoms. What is the electronic nature of such quasi-periodic systems, especially when compared to alternatives, which may or may not possess translational periodicity? In this communication, we shall select a series of linear chains with one orbital per site to model the three cases: periodic, quasi-periodic, and random. We shall analyze the eigenvalue spectra of these model systems and examine their structural stability as a function of electron count.

The model linear chains consist of a single orbital per site. Examples include the π manifold of polyacetylene and the mixed-valence platinum-chain compounds. The energy levels were obtained with use of simple Hückel theory. Since we are interested in energy differences between structures, all the Coulomb integrals α_i are set equal to zero as these parameters only affect the average energy of the band. Also, only nearest-neighbor interactions are included in the model. These Hückel β values will depend on the relevant internuclear separations within the chains.

Four types of linear chains from the three categories were selected as models. For a quasi-periodic system, the chain consists of two basic length scales, L and S, between adjacent atoms arranged in the sequence

SLSSLSLSSLSSL...
(I)

(this scheme represents the sequence of bond lengths within the chain). The motiviation for choosing this type of structure arises from its numerical similarities to the original Penrose tiling.[3] This tessellation fills two-dimensional space using four different shapes and generates a pattern that never repeats itself, i.e. possesses no translational periodicity. In addition, one can find five interpenetrating sets of parallel lines passing through all vertices with spacings in the ratio τ:1 ($\tau \equiv (5^{1/2} + 1)/2 = 1.61803...$; the golden mean)[4] and their sequence described by an algorithm using the Fibonacci series. Our "Fibonacci chain" uses the same algorithm with the ratio of the number of S lengths to the number of L lengths for the infinite case also in the ratio τ:1. For internal consistency the remaining chain models are limited to a maximum of two different length scales. We examine two types of translationally periodic chains for comparison with the quasi-periodic system. The first example contains one orbital per unit cell—the well-understood linear chain with equal distances between nearest neighbors.[5] The other example, containing 13 orbitals per unit

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