

The lowest energy ionization in the  $U[(CH_3)_5C_5]_2(CH_3)_2$  spectrum ( $x$ ) is assigned, as in the uranium dichloride, to the  $^2F_{5/2}$  final state component derived from the  $5f^2$  ground-state configuration. The other spin-orbit component,  $^2F_{7/2}$ , expected for a one-electron ionization of the  $U(IV)$   $^3H_4$  ground term, is not observed. The probability of reaching this state is small,<sup>3</sup> and the weak transition is likely to be obscured by other spectral features. There is also no evidence of ligand field splitting of the  $x$  transition. With the exception of  $U(C_5H_5)_3BH_4$ ,<sup>4b</sup> such effects have been too small to be observed in organouranium PE spectra.<sup>3,4</sup> The  $5f^2$  ionization in the uranium dimethyl compound is at lower energy than in the dichloride, as expected because of the electron-releasing properties of the  $\sigma$ -bonded methyl groups. However, the IE difference ( $\Delta IE = 0.21$  eV) is much smaller than would have been expected from considering a similar  $d^2$  system. For instance, on passing from  $Mo(C_5H_5)_2Cl_2$ <sup>12b</sup> to  $Mo(C_5H_5)_2(CH_3)_2$ <sup>22</sup> the IE shift of the  $d^{-1}$  ionization is 2.5 eV. Although the smaller organoactinide  $\Delta IE$  may reflect  $\pi$  bonding involving chlorine lone pairs, an equally plausible explanation can be advanced in terms of extraatomic relaxation in the  $^2F_{5/2}$  ion state. Namely, the electrostatic polarization of the nonbonding electron density of chlorine groups by the strongly localized positive hole produced upon ionization of  $5f$  subshells stabilizes the  $^2F_{5/2}$  state to a greater degree.

### Conclusions

This study provides the first comparison of He I/He II PE spectra for a series of transition-metal and actinide organometallic compounds with an identical ligand array. The most striking result of this comparison is that the spectra, hence many of the bonding characteristics, are so similar. To put this similarity in perspective, it is instructive to contrast the rather modest differences in orbital

ionization energies observed in the present series with the changes observed in the series  $Zr(C_5H_5)_2Cl_2$ ,  $Nb(C_5H_5)_2Cl_2$ ,  $Mo(C_5H_5)_2Cl_2$ .<sup>12a</sup> As the  $d^0$ ,  $d^1$ ,  $d^2$  series is traversed, far more drastic changes are observed. There is a reversal in level ordering with the ionization energy of the predominantly ring  $\pi$  orbitals increasing by ca. 1.5 eV and the ionization energy of the predominantly halogen  $3p$  orbitals falling by ca. 1.5 eV. These trends reflect major changes in the metal orbital energies and metal-ligand bonding which are not observed in the Zr, Th, U series.

Differences within the Zr, Th, U series are observed. Within the  $M[(CH_3)_5C_5]_2Cl_2$  group, there is some evidence for  $\pi$  interaction between Cl  $3p$ -based  $b_1(\pi)$  MOs and actinide  $5f_{xyz}$  orbitals. While there appears to be no corresponding, conspicuous interaction with the  $(CH_3)_5C_5^-$   $\pi$  MOs in the dichlorides, the situation appears opposite in the actinide  $M[(CH_3)_5C_5]_2(CH_3)_2$  compounds. Here, the methyl substituents are not suited for a  $\pi$  dative interaction with the metal ions, and possible as a consequence, the deviation from the zirconium system is this time observed in the ring  $\pi$  MO ionizations. Further investigations in this area, including calculations,<sup>24</sup> are in progress.

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## The Ambidentate Thiocyanate Ligand. Niobium-93 Nuclear Magnetic Resonance Detection of (Thiocyanato)- and (Isothiocyanato)niobium(V) Complexes

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**Abstract:** Niobium-93 NMR investigation of acetonitrile solutions containing six-coordinate niobium(V) complexes with thiocyanate ion and chloride ion ligands has revealed 16 magnetically nonequivalent niobium environments (i.e., different complexes) within a chemical shift range of 1342 ppm. Use of the pairwise additivity model has enabled the assignment of these spectral lines to 16 of the 56 different configurations possible for the system  $[Nb(NCS)_n(SCN)_mCl_{6-(n+m)}]^-$ . The ligand redistribution reaction which gives rise to these complexes produces both S-bonded and N-bonded thiocyanate complexes with about equal frequency. The previously unreported  $[Nb(SCN)_6]^-$  represents the first case of a homogeneous complex in which thiocyanate ion bonds through its sulfur atom to a class metal. Some new questions are raised about the hard-soft acid-base generalization for chemical bonding.

The study here reported deals with a metal-ligand system made highly complex by virtue of linkage isomerism, with a novel spectroscopic technique the discriminating power of which matches the complexity of the system under study, and with the limitations to a metal-ligand bonding generalization that has come to enjoy widespread currency among inorganic chemists.

**The Metal-Ligand System.** The pioneering work of Werner on cobalt complexes done in the early part of this century established the beauty, symmetry, and simplicity of six-coordination. If the six ligands surrounding a metal atom are of three different types, however, much of the simplicity disappears. A complex

$MX_2Y_2Z_2$  has 5 geometric isomers, and if the lability of this complex in solution gives intermolecular redistribution of ligands, the resulting system of  $MX_nY_mZ_{6-(n+m)}$  complexes permits 28 different stoichiometries encompassing 56 different configurations. The niobium(V) complexes reported in this study undergo slow ligand redistribution to give an equilibrium mixture of identifiably discrete configurations in solution, all belonging to the  $[Nb(NCS)_n(SCN)_mCl_{6-(n+m)}]^-$  system.

**Pairwise Additivity and <sup>93</sup>Nb Chemical Shifts.** There are few analytical techniques capable of identifying the presence of one specific configuration in a solution mixture which may contain

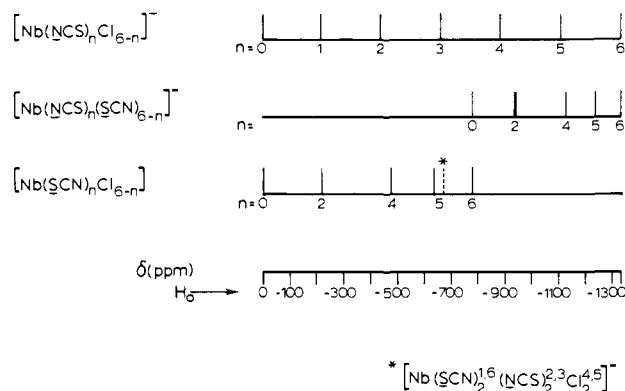
Table I.  $^{93}\text{Nb}$  Chemical Shifts in Parts per Million and Line Shapes for Eight Solutions Containing  $[\text{Nb}(\text{NCS})_n(\text{SCN})_m\text{Cl}_{6-(n+m)}]^-$  Species in Acetonitrile or 1,2-Dichloroethane<sup>a</sup>

A	B	C	D	E	F	F'	G
0 ss			0 ss	0 ss	0 ss	0 ss	0 ss
-233 mm	-220 mb		-230 mm				
	-457 mb	-233 mm	-461 wm				
-475 mm		-456 sm					
-633 sm		-633 sm	-630 sm		-630 mm		
	-670 ss						
-681 ms		-680 vs, s	-683 ms				
-781 vss	-781 ms	-780 ms	-780 ms	-780 vss	-780 ms	-780 vss	
	-902 s, vb	-902 m, vb			-902 vs, m		
-947 mb			-940 sm	-940 sm			
			-1117 sm	-1115 sm	-1120 sm	-947 sm	
-1125 mb	-1125 mb	-1125 bm				-1120 mm	
					-1235 mm		
-1342 ws	-1342 ms	-1342 ms	-1342 ss	-1342 ss	-1342 ms	-1342 ws	-1342 vss

<sup>a</sup> Solution compositions: A,  $\text{NbCl}_5 + \text{KSCN}/\text{MeCN}$ ; B,  $\text{KNb}(\text{NCS})_6 + \text{NbCl}_5/\text{MeCN}$ ; C,  $\text{KNb}(\text{NCS})_6 + \text{NbCl}_5 + \text{KCl}/\text{MeCN}$ ; D, as C with excess  $\text{NbCl}_5$ ; E,  $\text{KNb}(\text{NCS})_6 + \text{Et}_4\text{NNbCl}_6/\text{MeCN}$ ; F,  $\text{PhAsNb}(\text{NCS})_6 + \text{Et}_4\text{NNbCl}_6/\text{MeCN}$ ; F', as F, 5 days at room temperature; G, as F in 1,2-dichloroethane. Line shape designations: intensity, vs = very strong, s = strong, m = medium, w = weak; line width, s = sharp, m = medium, b = broad.

up to 56 components. The presence of both N-bonded and S-bonded thiocyanate *within the same molecule* has traditionally been postulated on the basis of infrared spectral evidence;<sup>1</sup> the spectral interpretation in unfavorable cases, however, is not without difficulties.<sup>2</sup> The first unambiguous report of this phenomenon is the X-ray structure determination of  $\text{Pd}[(\text{C}_6\text{H}_5)_2\text{PCH}_2\text{CH}_2\text{C}-\text{H}_2\text{N}(\text{CH}_3)_2](\text{SCN})(\text{NCS})$  reported by Clark and Palenik.<sup>3</sup> The pairwise additivity model<sup>4</sup> for  $^{93}\text{Nb}$  NMR chemical shifts predicts that most of the 56 configurations in the system under study will be separated from each other by at least 7 ppm. Since lines in the  $^{93}\text{Nb}$  NMR spectrum of the mixture can be located to within  $\pm 2$  ppm, this technique enables the identification of those species actually present in solution.

**The Hard-Soft Acid-Base Model.** It is the unexpected that most fascinates the scientist, and ambidentate ligands hold great potential for the unexpected. The thiocyanate ion, because of its ability to form both S-bonded (thiocyanato) and N-bonded (isothiocyanato) complexes, has provided material for much speculation about the bonding interaction in coordination complexes. The hard-soft picture of acids and bases developed by Pearson<sup>5,6</sup> is the theoretical model with which most of this speculation has been conducted, and although the model has been criticized for lacking finesse,<sup>7</sup> its inherent generality is sufficiently appealing that it continues to form the basis for predicting the behavior of ambidentate ligands. This model predicts that when a hard metal atom such as niobium(V) is coordinated only by an ambidentate thiocyanate ligand, the isothiocyanato complex with bonding to the hard N-atom rather than the thiocyanato complex with bonding to the soft S-atom will be favored. It is the later or class *b* transition metals, particularly Ir, Pd, Pt, Ag, Au, and Hg, which are regarded as being soft. While the incidence of S-bonded thiocyanate is lower than that of N-bonded, thiocyanato complexes of Rh,<sup>9</sup> Ir,<sup>9</sup> Pd,<sup>9</sup> Pt,<sup>9</sup> Co,<sup>10</sup> Ag,<sup>23</sup> Au,<sup>24</sup> Cd,<sup>8</sup> and Hg<sup>8</sup> have been well documented. Reports based solely upon infrared evidence of S-bonding to Cr<sup>11,12</sup> and V<sup>13</sup> have appeared, but the

 $^{93}\text{Nb}$  Spectra for  $[\text{Nb}(\text{NCS})_n(\text{SCN})_m\text{Cl}_{6-(n+m)}]^-$  SpeciesFigure 1. Assignment of  $^{93}\text{Nb}$  Spectral Lines among the Three Families of Binary Complexes and the One Ternary Complex Family

unreliability of  $\nu_{\text{CN}}$  as a criterion for coordination mode means that a final judgement must await confirmation by NMR spectroscopy, UV-visible spectroscopy, or an X-ray structure determination. The transition metals with lower periodic group numbers are increasingly hard, and Norbury's comprehensive review of thiocyanate complexes<sup>14</sup> shows that the earliest transition metals for which a thiocyanato isomer has been characterized are manganese  $[\text{Mn}(\text{CO})_5(\text{SCN})]$ , molybdenum  $[\eta^5\text{-CpMo}(\text{CO})_3(\text{SCN})]$ , and tungsten  $[\eta^5\text{-CpW}(\text{CO})_3(\text{SCN})]$ , and the low oxidation state of the metal in each case removes it from the "hard" classification. The  $[\text{Nb}(\text{SCN})_6]^-$  and related thiocyanato complexes in this study represent the first report of a homogeneous complex containing thiocyanate S-bonded to an undeniably class a or hard metal. In the niobium(V) isomer mixtures studied, S-bonded and N-bonded thiocyanate occur with about equal frequency, and several instances of S-bonded and N-bonded thiocyanate in the same coordination complex are observed. The fact that, in its bonding to niobium(V), the thiocyanate ion exhibits no strong preference for either bonding mode raises some inter-

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esting questions about the hard-soft metal-ligand generalization.

### Results and Discussion

The  $^{93}\text{Nb}$  NMR line positions obtained from seven different niobium(V)-containing solutions are reported in Table I. The composition of each solution is given at the bottom of the table. The highest field peak at  $-1342$  ppm relative to  $\delta_{\text{NbCl}_6^-} = 0$  appears for every solution and indicates the presence of N-bonded  $\text{Nb}(\text{NCS})_6^-$ . Most of the other peaks have been observed for more than one solution, and in all, 16 different peaks having a signal-to-noise ratio greater than 2:1 have been observed. The relative positions of these lines are recorded in Figure 1, which shows that 15 of them belong to one of the three families of binary complexes, while the  $-670$ -ppm peak is assignable to the only ternary complex to be observed.

**Spectral Assignments.** The pairwise additivity model for predicting the metal atom shielding in an octahedral complex rests on the assumption that the pair of ligands constituting an edge of the octahedron makes an independent contribution to the metal atom shielding. These pairwise ligand effects  $\eta_{ij}$ , summed over the 12 edges of the octahedron, determine the metal shielding, and its chemical shift, in parts per million, is given by  $\delta = \sum C_{ij} \eta_{ij}$  ( $0 \leq C \leq 12$ ), where the coefficient  $C$  specifies the number of times a specific ligand pair edge occurs in the complex. Since three ligands can be combined pairwise in six different ways, there are six initially unknown  $\eta_{ij}$  parameters to be evaluated. If the assignments of all spectral lines were known, then six different line positions would suffice to evaluate all  $\eta_{ij}$ . Because independent assignments are not available, a narrowing down process culminating in multiple regression analysis must be employed.

Previous work<sup>4,15</sup> has established that in the presence of excess halide ion and in acetonitrile solution, the niobium(V) atom exists solely as molecular, monomeric, anionic, octahedral  $\text{NbX}_6^-$  species. In particular, halogen-bridged dimers are not present and neutral species of the type  $[\text{NbX}_5 \cdot \text{CH}_3\text{CN}]$  are only formed (with great difficulty) under rigorously anhydrous conditions and in the strict absence of excess halide ion. While Il'in et al.<sup>27</sup> report the presence of  $[\text{Nb}(\text{NCS})_7]^{2-}$  in similar solutions, no evidence of seven-coordinate species was observed in our spectra.

Where two different halides are present, the redistribution reaction yields the system  $[\text{NbX}_n\text{Y}_{6-n}]^-$  which contains seven different stoichiometries, three of which have two geometric isomers, for a total of ten different molecules. In the present niobium(V) system involving chloride ion and thiocyanate ion as ligands, 16 distinct resonance lines representing 16 different magnetic environments for the niobium nucleus are observed. From this we deduce that sulfur-bonded as well as nitrogen-bonded thiocyanate *must* be present after redistribution, giving us, in effect, the three-ligand system  $[\text{Nb}(\text{NCS})_n(\text{SCN})_m\text{Cl}_{6-(n+m)}]^-$ .

In acknowledging the presence of a three-ligand pseudooctahedral coordination complex, one is faced with a large number of possible stoichiometries and geometric configurations. For purposes of discussion, these will be divided into class I types in which all six ligands attached to a niobium atom are the same, class II types in which all six ligands are of two types, and class III types in which Cl, SCN, and NCS ligands are all represented among the six coordination positions on a given niobium atom. Summarized briefly, the numbers in each class are as follows.

complex type	no. of stoichiometries	no. of configurations
class I	3	3
class II	15	24
class III	10	29
total	28	56

Each of these 56 configurations will in principle give a separate  $^{93}\text{Nb}$  resonance, and previous work<sup>4</sup> indicates that each is capable of resolution. The method whereby each of the 16 observed resonances is assigned to one of the 56 configurations involves four distinct steps. (i) The recognition of those configurations for which

$^{93}\text{Nb}$  resonance assignments have already been made in a previous study. (ii) The recognition that substitution of an S-bonded for an N-bonded thiocyanate ion causes a marked downfield shift in the  $^{93}\text{Nb}$  resonance. (iii) Calculation of an *approximate* chemical shift value for each of the 28 stoichiometries assuming a linear substitution-shielding relationship. (iv) The use of a multiple linear regression analysis to obtain the best set of six pairwise additivity parameter values from the 16 observed line positions. These in turn yield a unique assignment to specific configurations of all 16 observed lines.

The resonance at 0 ppm is assigned to the known reference species  $[\text{NbCl}_6]^-$ . The resonance at  $-1342$  ppm (Table I) is the sole resonance observed in solutions reported<sup>15,16</sup> to contain  $[\text{Nb}(\text{NCS})_6]^-$  and is so assigned. The resonance at  $-780$  ppm is assigned<sup>17</sup> to  $[\text{Nb}(\text{SCN})_6]^-$  for two reasons. The degree to which a metal nucleus is magnetically shielded by an attached ligand is related to the position of that ligand in the *nephelauxetic* series.<sup>18</sup> This assignment is consistent with the position of SCN between Cl and NCS in the *nephelauxetic* series. In addition, the  $-780$ -ppm line is consistently sharp in all the spectra, requiring a high degree of geometric symmetry as is present in  $[\text{Nb}(\text{SCN})_6]^-$ .

An *approximation* to the degree of shielding experienced by the niobium nucleus was obtained for all 28 possible stoichiometries on the rough assumption that there is a direct substituent-shielding correlation. This linear approximation (first-order) method and its results, based upon the observed shift values for  $[\text{NbCl}_6]^-$ ,  $[\text{Nb}(\text{SCN})_6]^-$ , and  $[\text{Nb}(\text{NCS})_6]^-$ , are employed as an empirical aid to effect assignment of *stoichiometries* to observed resonances. It has been recognized,<sup>4,19</sup> however, that the nuclear shielding of a metal atom is not strictly a linear function of substitution but depends upon both ligand-metal and ligand-ligand interactions. This dependence has been satisfactorily represented by the pairwise additivity model which enables one to calculate the chemical shift for a central atom by the summing of pairwise interaction parameters for all substituents taken as adjacent pairs. It is precisely because of this second-order dependence that a distinction can be made among the various geometric isomers comprising a particular stoichiometry, thus permitting assignment of specific configurations to observed resonance lines.

By first analyzing each of the binary ligand families and then the ternary ligand family in this stepwise manner, we obtained  $\eta$  values at each stage to facilitate assignment of the remaining resonances. This process yielded the set of linear equations comprising the matrix presented in Table II. Treatment of the entire matrix by linear regression analysis produced solutions for the  $\eta_{ij}$  consistent with those obtained in the preliminary partial analysis. The validity of the assignments in Table II is confirmed by the close correspondence of  $\delta_{\text{calcd}}$  and  $\delta_{\text{obsd}}$  values.<sup>20</sup> Although calculated shift values are not presented for all 56 possible configurations, they may readily be determined by a summation of  $C_{ij}\eta_{ij}$  products describing the particular configuration.

**The Hard-Soft Acid-Base Model.** The linkage isomerism of ambidentate ligands having both a hard and a soft basic atom has traditionally served as a test for the hard-soft acid-base generalization, and thiocyanate complexes have heretofore provided the most consistent pattern in support of the model. For complexes where thiocyanate ion is the only ligand present, the mode of coordination and the complexes formed are shown in Table III. With use of the original Ahrland, Chatt, and Davies classification<sup>25</sup> (class a contains Sc, Y, La, Ti, Zr, Hf, V, Nb, Ta, and Cr; class b contains Ir, Pd, Pt, Ag, Au, and Hg), these data provide no

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Table II. Matrix Coefficients, Pairwise Interaction Parameters, and Calculated and Observed  $^{93}\text{Nb}$  Line Positions for  $[\text{Nb}(\text{NCS})_n(\text{SCN})_m\text{Cl}_{6-(n+m)}]^-$  Species

species	coeff $C_{ij}$						$\delta_{\text{calcd.}}^a$ $\sum C_{ij}\eta_{ij}$	$\delta_{\text{obsd.}}$ ppm
	Cl-Cl	S-S	N-N	Cl-S	Cl-N	S-N		
$\text{NbCl}_6$	12	0	0	0	0	0	-2	0
$\text{NbCl}_5\text{N}^b$	8	0	0	0	4	0	-230	-232
$\text{NbCl}_4\text{N}_2$ (cis)	5	0	1	0	6	0	-456	-457
$\text{NbCl}_3\text{N}_3$ (cis)	3	0	3	0	6	0	-679	-681
$\text{NbCl}_2\text{N}_4$ (cis)	1	0	5	0	6	0	-902	-902
$\text{NbClN}_5$	0	0	8	0	4	0	-1122	-1118
$\text{NbN}_6$	0	0	12	0	0	0	-1341	-1342
$\text{NbS}_6$	0	12	0	0	0	0	-782	-780
$\text{NbS}_5\text{N}_2$ (cis)	0	5	1	0	0	6	-946	-947
$\text{NbS}_4\text{N}_2$ (trans)	0	4	0	0	0	8	-939	-940
$\text{NbS}_2\text{N}_4$ (trans)	0	0	4	0	0	8	-1125	-1125
$\text{NbSN}_5$	0	0	8	0	0	4	-1234	-1235
$\text{NbS}_2\text{Cl}_4$ (trans)	4	0	0	8	0	0	-217	-220
$\text{NbS}_4\text{Cl}_2$ (trans)	0	4	0	8	0	0	-477	-475
$\text{NbS}_5\text{Cl}$	0	8	0	4	0	0	-630	-633
$\text{NbS}_2^{1,6}\text{N}_2^{2,3}\text{Cl}_2^{4,5}$	1	0	1	4	2	4	-674	-670

<sup>a</sup> Values for pairwise interaction parameters in parts per million obtained from regression analysis of this matrix are  $\eta_{\text{Cl-Cl}} = 0.0$ ,  $\eta_{\text{SCN-SCN}} = -65.0$ , and  $\eta_{\text{NCS-NCS}} = -111.5$ . <sup>b</sup> N = NCS ligand; S = SCN ligand.

Table III. Incidence<sup>a</sup> of N-Bonded and S-Bonded Linkage Isomerism among Homogeneous Thiocyanate Complexes of the Transition Metals

$\text{VN}_6^{3-}$	$\text{CrN}_6^{3-}$	$\text{MnN}_4^{2-}$	$\text{FeN}_4^{2-}$	$\text{CoN}_4^{2-}$	$\text{NiN}_4^{2-}$	$\text{CuN}_4^{2-}$	$\text{ZnN}_4^{2-}$
$\text{NbN}_6^{2-}$	$\text{MoN}_6^{2-}$	$\text{MnN}_6^{4-}$	$\text{FeN}_6^{3-}$		$\text{NiN}_6^{4-}$		$\text{ZnN}_6^{4-}$
$\text{NbN}_6^{2-}$	$\text{MoN}_6^{3-}$	$\text{TeN}_6^{2-}$	$\text{RuN}_6^{3-}$	$\text{RhS}_6^{3-}$	$\text{PdS}_4^{2-}$	$\text{AsS}_2^-$	$\text{CdN}_2\text{S}_2^{2-}$
$\text{TaN}_6^{3-}$	$\text{WN}_6^{2-}$	$\text{ReN}_6^-$	$\text{OsN}_6^{3-}$	$\text{IrS}_6^{3-}$	$\text{PtS}_4^{2-}$	$\text{AuS}_4^-$	$\text{CdN}_6^{4-}$
	$\text{WN}_6^{3-}$	$\text{ReN}_6^{2-}$			$\text{PtS}_6^{2-}$		$\text{HgS}_4^{2-}$

<sup>a</sup> On the basis of critical literature review contained in ref 14.

exceptions to the class a-N-bonded, class b-S-bonded rule. It is only in mixed-ligand complexes that S-bonded thiocyanate has been obtained with metals lying to the left of iridium in the periodic table, and in these cases electronic effects arising from the other ligand are deemed to "soften" the class a metal making it amenable to S-bonding.

In this study, not only does  $[\text{Nb}(\text{SCN})_6]^-$  occur at concentrations comparable with those of  $[\text{Nb}(\text{NCS})_6]^-$  in most of the solutions, but the intermediate complexes  $n = 2, 4$ , and 5 in the binary ligand family  $[\text{Nb}(\text{NCS})_n(\text{SCN})_{6-n}]^-$  occur as well in at least one of the solutions studied. Without speculating about the details of why the  $n = 1$  and 3 complexes are not formed, one can make the general observation that *in solution* the incidence of S-bonding to niobium(V) is comparable with that of N-bonding. This requires a Nb-S interaction of strength comparable with that of the Nb-N interaction and weighs against the Pearson model that would have the hard niobium(V) discriminate in favor of the hard N-atom by forming a stronger bond.<sup>22</sup>

Had this observation been made for ruthenium or technetium which lie in the border line region between the class a and class b metals, the impact upon the hard-soft bonding model would not be particularly disquieting, but niobium lies four periodic groups to the left of rhodium, the "last" transition metal to form a homogeneous S-thiocyanate complex. Its occurrence in the heart of class a territory forces a reexamination of the hard-soft acid-base generalization. Is it possible that the preponderance of N-bonded isothiocyanate complexes in Table III reflects a solubility difference leading to precipitation of the N-bonded isomer from an equilibrium mixture of the two rather than an

enthalpic difference in the metal-ligand bond strength? Since the M-N-C bond angle is linear, while the M-S-C angle is bent, a consistent solubility difference would not be surprising. The resolution of this question requires the study in solution of the linkage isomers formed by thiocyanate ion with metals other than niobium.

Burmeister et al.<sup>28</sup> have shown that the N-bonded  $\rightleftharpoons$  S-bonded isomerization equilibrium for thiocyanato complexes in solution is solvent dependent and that acetonitrile favors S-bonded complexes. If the  $[\text{Nb}(\text{SCN})_6]^-$  observed in this study represents a case of solvent control of bonding mode, then solvent becomes the first-order determinant of complex stability and the hard-soft acid-base principle becomes a second-order effect for complexes *in solution*.

### Experimental Section

Niobium-93 NMR spectra were obtained at 14.67 MHz by using a Varian 4200 B wide-line spectrometer with a V-4210 A variable-frequency oscillator and a V-3400 9-in. magnet with Fieldial stabilization and sweep capability. Resonance lines were recorded as derivatives of dispersion signals, and calibration was effected by the generation of audiofrequency sidebands. Minimum detection sensitivity for niobium species under these conditions is about 0.05 M. Chemical shift values, designated by  $\delta$ , are quoted in parts per million (ppm) relative to the  $[\text{NbCl}_6]^-$  signal, with positive shifts denoting decreased shielding. All spectra were measured at room temperature. Quoted errors in  $\delta$  values are standard deviations and result from calibration uncertainty.

The solvents (acetonitrile and 1,2-dichloroethane) used in this study were rigorously dried by prolonged reflux over, and fractional distillation from, calcium hydride while under a dry-nitrogen atmosphere. High-purity niobium pentachloride from Alfa Inorganics was used as the niobium source in all preparations. The only potential impurities of concern were those that might affect the NMR spectra, and these were checked by obtaining their  $^{93}\text{Nb}$  spectra. Niobium's high affinity for oxygen puts the oxyhaloniobates in this category, so they were prepared and their line positions in acetonitrile solution found to be  $\text{NbOCl}_3$  at  $\delta -503$ ,  $[\text{NbOCl}_{3+n}]^{n-}$  ( $n \approx 2$ ) at  $\delta -482$ , and  $[\text{NbOBr}_{3+n}]^{n-}$  ( $n \approx 2$ ) at  $\delta -200$ . Buslaev et al.<sup>26</sup> have characterized this system in greater detail. Tetraethylammonium hexachloroniobate(V) was prepared by the accepted

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method<sup>21</sup> using redistilled thionyl chloride as solvent. The hexakis(thiocyanato)niobate(V) salts were prepared by using the method of Knox and Brown.<sup>15</sup>

The actual solutions that were used for spectroscopic study are described in Table I. All solutions were prepared as concentrated or saturated solutions with a niobium concentration in the range 0.5-1 M. The Cl:NCS:Nb ratios were generally 3:3:1, although these were varied from 5:1:1 to 1:5:1 in an attempt to detect additional resonance lines. All

redistribution solutions, which were deep red in color, required one to several hours at room temperature to attain final equilibrium. Redistribution did not occur in 1,2-dichloroethane, and this was likely a function of the low dielectric constant of this solvent.

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## Iron(II, III)-Chlorin and -Isobacteriochlorin Complexes. Models of the Heme Prosthetic Groups in Nitrite and Sulfite Reductases: Means of Formation and Spectroscopic and Redox Properties

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**Abstract:** Extensive series of iron(II, III)-hydroporphyrin complexes of the types Fe(P)L, [Fe(P)LL']<sup>0+</sup>, [Fe(P)]<sub>2</sub>O, and Fe(P), with P = octaethylchlorin (OEC) and octaethylisobacteriochlorin (OEiBC) and L, L' = neutral or uninegative axial ligands, have been synthesized and isolated or generated in solution. Means of synthesis and reactivity properties of OEC and OEiBC complexes parallel those of octaethylporphyrin (OEP) complexes. This behavior, together with a detailed body of physicochemical properties (absorption, MCD, <sup>1</sup>H NMR, EPR, and infrared spectra and voltammetry), serves to identify all new complexes. Certain of the OEiBC species are pertinent as possible analogues of the siroheme prosthetic group of nitrite and sulfite reductases. Physicochemical properties of OEP, OEC, and OEiBC complexes at parity of axial ligation are compared in an attempt to identify any intrinsic features of isobacteriochlorin species that might render them particularly suitable for mediation of multielectron reductions of substrates as executed by siroheme enzymes. Properties such as Fe(III)/Fe(II) potentials and  $\nu_{\text{CO}}$  of Fe(P)L(CO) and Fe(P)(CO)<sub>1,2</sub> were found to be nearly invariant to P, indicating little cis effect of these macrocycles, which are in different reduction levels. That property most dependent on macrocycle structure was found to be the potential for ring-based oxidation which increases in the order OEiBC < OEC < OEP. Comparative properties are discussed in some detail and are related to available information on sirohemes, including the question of axial ligation in the native enzyme. This research affords the first comprehensive examination of the preparation and chemical, spectroscopic, and redox properties of iron(II, III)-hydroporphyrin complexes.

A substantial body of evidence now exists for a variety of heme-containing proteins and enzymes that demonstrates the presence of iron-hydroporphyrin prosthetic groups. Some dissimilatory nitrite reductases, which catalyze the reduction of NO<sub>2</sub><sup>-</sup> to NO, contain heme *d*,<sup>2-8</sup> an iron-chlorin complex.<sup>9</sup> Assimilatory nitrite reductases as well as assimilatory and dissimilatory sulfite reductases, which catalyze the remarkable six-electron reductions NO<sub>2</sub><sup>-</sup> + 7H<sup>+</sup> + 6e<sup>-</sup> → NH<sub>3</sub> + 2H<sub>2</sub>O and SO<sub>3</sub><sup>2-</sup> + 6H<sup>+</sup> + 6e<sup>-</sup> → S<sup>2-</sup> + 3H<sub>2</sub>O, respectively, possess as a common prosthetic group an iron-isobacteriochlorin complex named siroheme.<sup>10-14</sup> This

unit has been removed from several enzymes and examined separately.<sup>11,13,15</sup> It can be demetallated to afford the free macrocycle, sirohydrochlorin, for which structure 1 has been proven.<sup>16</sup> Spectroscopic studies of a number of enzymes,<sup>12-14,17-20</sup> especially of the assimilatory type, leave little doubt that siroheme is the substrate binding and activating site. Siroheme has also been detected in enzymes for which sulfide oxidase activity, i.e., the oxidation of sulfide to sulfite, has been proposed.<sup>21</sup>

Despite the seemingly obligatory presence of siroheme in the enzymes responsible for two of only three known six-electron

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