Table I. Range of Sn–X Stretching Frequencies for Some $SnX_4 \cdot 2L$ Complexes

SnX_4	Ligand[a]	Classification	Range of ν(Sn–X) absorption, cm^{-1}	Ref
cis-$SnCl_4$	DME	Hard	340–325	5
	2 AA	Hard	341–305	6
	2 DMF	Hard	340–313	7
	TMEN	Hard	325–300	8
	bipy	Borderline	333–284	9
	phen	Borderline	341–278	9
	PN	Borderline[b]	325–309	10
	DP	Soft	323–305	10
	diphos	Soft	320–297	9
	DTH	Soft	326–288	9
trans-$SnCl_4$	2 THF	Hard	342	4
	2 DAA	Hard	328	6
	2 py	Borderline	323	4
	2 THT	Soft	318	4
	2 TPA	Soft	309	4
	2 TPP	Soft	307	4
cis-$SnBr_4$	DME	Hard	250–220	5
	2 DMF	Hard	249–216	7
	TMEN	Hard	230–209	8
	bipy	Borderline	258–218	9
	phen	Borderline	244–226	9
	PN	Borderline[b]	216–203	10
	DP	Soft	234–208	10
	diphos	Soft	233–207	9
	DTH	Soft	246–216	9
trans-$SnBr_4$	2 THF	Hard	247	4
	2 py	Borderline	247, 231	4
	2 THT	Soft	218	4
	2 TPP	Soft	209	4
cis-SnI_4	TMEN	Hard	170–136	8, 11
	2 HQ	Hard[c]	178–140	12
	bipy	Borderline	196–173	9
	phen	Borderline	195–191	9
	PN	Borderline[b]	194–139	10
	DP	Soft	205–167	10
	diphos	Soft	190–180	8
	DTH	Soft	182–170	9
trans-SnI_4	2 $N(CH_3)_3$	Hard	158–142	11
	2 py	Borderline	195–185	4

[a] Abbreviations: DME, 1,2-dimethoxyethane; AA, acrylamide; DMF, *N,N*-dimethylformamide; TMEN, *N,N,N',N'*-tetramethylethylenediamine; bipy, 2,2'-bipyridyl; phen, 1,10-phenanthroline; PN, *o*-$C_6H_4(PPh_2)N(CH_3)_2$; DP, *o*-$C_6H_4(PPh_2)_2$; diphos, 1,2-bis(diphenylphosphino)ethane; DTH, 2,5-dithiahexane; THF, tetrahydrofuran; DAA, *N,N*-dimethylacrylamide; py, pyridine; THT, tetrahydrothiophene; TPA, triphenylarsine; TPP, triphenylphosphine; HQ, 8-hydroxyquinoline. [b] The molecule contains a hard and soft donor and is arbitrarily classified as borderline. [c] Coordination through oxygen assumed; stereochemistry not assigned.

on $SnCl_4$ decreased in the order $PPh_3 > AsPh_3 > THT > py > THF$ (where THT = tetrahydrothiophene).

This order appears to be the opposite of what would be predicted according to HSAB principles. Tin(IV) in $SnCl_4$ is hard and would be expected to form the strongest bond with THF; i.e., the reverse order of force constants from that shown above would be expected.

However, if one examines the Sn–X stretching frequencies with respect to the nature of the other donor ligands, then a result consistent with HSAB theory is observed. Table I shows the pertinent data.

Upon examination of the range of absorption of ν(Sn–X) one observes that, for $SnCl_4$ complexes, the Sn–Cl frequencies are highest where the coordinated ligands are hard, intermediate with borderline ligands, and lowest where soft donors are coordinated. This is true for both cis and trans complexes. The $SnBr_4$ complexes are not quite as clear-cut, where the Sn(IV) acid center in these complexes would be expected to be somewhat softer than in the tetrachloride. For $SnBr_4$ complexes, it is the general trend that the strongest Sn–Br bond strength occurs in the presence of hard and borderline bases. The SnI_4 complexes, where the acid center is still softer than the others, shows the highest Sn–I absorption where the coordinated ligands are borderline or soft.

It is clear, therefore that for *cis*- and *trans*-$SnCl_4L_2$ and -$SnCl_4LL$ complexes, the Sn–Cl stretching frequencies decrease in the order of coordinated ligand: hard > borderline > soft. For the corresponding bromide complexes, the order appears to be hard ~ borderline > soft. Whereas there exists a paucity of infrared spectral information on complexes of SnI_4 with hard bases, for those few examples reported, the trend for the corresponding iodide complexes is opposite that of the chloride complexes, i.e., hard < borderline ~ soft.

Whereas the observation made by Ohkaku and Nakamoto that the SnX bond becomes stronger as the SnL bond becomes weaker may hold, the more useful statement (for prediction and band assignment purposes) may be made that the tin–halide stretching frequencies will be higher where the coordinated ligand is more like the halide in terms of hardness or softness.

Registry No. Tin, 7440-31-5.

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Atomization Enthalpy of Europium Trichloride

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Sir:

In a recent note on bonding models for lanthanide trihalides,[1] the calculated enthalpy for the reaction

$$EuCl_3(g) = Eu^*(g) + 3Cl(g) \quad \Delta H_{at}^* = 387 \text{ kcal/mol} \tag{1}$$

was noted to be anomalously high. It has been pointed out[2] that the difficulty lies with the value of the enthalpy of formation of $EuCl_3(s)$ used in calculating ΔH_{at}^* and *not* with the enthalpy of sublimation of europium[3] nor with the promotion energy ($d^2s \leftarrow$ ground state) of the europium atom.[4] When the more recent and reliable value,[5] $\Delta H_f°(EuCl_3(s)) = -223.7$ kcal/mol, is used, a revised value of the enthalpy of reaction 1, $\Delta H_{at}^* = 364$ kcal/mol, is obtained which removes the apparent anomaly. The irregularities in ΔH_{at}^* for EuX_3 (X = F, Br, I) molecules are due to an error in the estimated enthalpies of formation[6] which assumed $\Delta H_f°(LnX_3(s))$ to vary smoothly across the lanthanide series.

In summary, the apparent anomaly in the values of $\Delta H_{at}^*(EuX_3)$ has been removed and there is no need to question either the enthalpy of sublimation of europium or the valence-state promotion energy of the europium atom.

Registry No. $EuCl_3$, 10025-76-0.

References and Notes

(1) C. E. Myers, *Inorg. Chem.*, **14**, 199 (1975).
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Additions and Corrections

1973, Volume 12

George F. McKnight and G. P. Haight, Jr.*: Reactions of Octacyanomolybdate(VI). I. Kinetics of Oxidation by Chromium(VI).

Pages 1619 and 1620. An error of sign in the exponent of the rate constant has been made in (1) the abstract, page 1619, $k = (8.3 \pm 2.0) \times 10^4$, (2) the last line before the **Discussion**, page 1620, $k = (8.8 \pm 1.5) \times 10^4$, and (3) the third column heading in Table III which should read $10^{-4}k''/[H^+]^2$. Parts of the discussion based on the reported low value of k are thus irrelevant since $Mo(CN)_8^{4-}$ is actually faster than $Fe(CN)_6^{4-}$, but the conclusions concerning inner sphere electron transfer processes are not affected.—G. Haight

1974, Volume 13

Daniel D. Poulin and Ronald G. Cavell*: Phosphoranes. I. Tris(trifluoromethyl)bis(dimethylamino)phosphorane, $(CH_3)_3P[N(CH_3)_2]_2$, and Related Chlorodimethylaminotrifluoromethylphosphoranes.

Page 2332. The first sentence after the bold face heading in column 1 should read: "The nmr results obtained herein and elsewhere[26] consistently suggest that CF_3 groups preferentially occupy equatorial positions in halogenophosphoranes even when the CF_3 group has a *higher* electronegativity than the halogen."—Ronald G. Cavell

Nick Serpone* and Ken A. Hersh: Kinetic Analysis of the Configurational Rearrangements in and the Stereochemistry of Some Organotin(IV) β-Ketoenolate Complexes.

Page 2905. In the second column, the sentence beginning on line 22 should read: "To describe this exchange process,.....six independent first-order rate constants will...".—N. Serpone

1975, Volume 14

Philip S. Bryan and James C. Dabrowiak*: Synthesis and Characterization of Manganese Complexes Containing a Synthetic Macrocyclic Ligand.

Page 297. In Table II, the column headings of the first and second columns should be interchanged, and the headings of the third and fourth columns should be interchanged.—James C. Dabrowiak

Fred W. Moore and Kenneth W. Hicks*: Mechanism of the Permanganate Ion Oxidation of Vanadium(IV).

Page 413. The middle initial of the first author should read "W".—Kenneth W. Hicks

D. L. Reger: Cyanide, Isocyanide, and Nitrile Derivatives of Cyclopentadienyliron. Interaction of Chiral Metal Complexes with an Optically Active Shift Reagent.

Page 662. Twenty lines were omitted from the top of the first column on page 662. Beginning with the last line on page 661, the text should read as follows:

2. Potassium Cyanide. A mixture of $[(\eta^5\text{-}C_5H_5)Fe(CO)(CNEt)(PPh_3)]PF_6$ (0.7 g, 1.15 mmol) and KCN (0.15 g, 2.3 mmol) was heated at 70° for 3 hr in ethanol (40 ml). As no reaction took place under these conditions, the solution was then refluxed for 2 hr. The infrared spectrum of this solution indicated that starting reagents were still mainly present with small amounts of $(\eta^5\text{-}C_5H_5)Fe(CO)(CN)(PPh_3)$ also present. More KCN (0.1 g, 1.5 mmol) was added and the solution was refluxed for 6 hr more. Additional $(\eta^5\text{-}C_5H_5)Fe(CO)(CN)(PPh_3)$ had formed, but the solution still contained mainly starting reagents.

3. Sodium Borohydride. A mixture of $[(\eta^5\text{-}C_5H_5)Fe(CO)(CNEt)(PPh_3)]PF_6$ (1.0 g, 1.6 mmol) and $NaBH_4$ (0.3 g, 7.9 mmol) was stirred for 2 hr in THF (40 ml). The solvent was evaporated, and the resulting residual oil was dissolved in benzene (8 ml) and chromatographed on alumina (2 × 8 cm) with hexane–diethyl ether (2:1 v/v) as eluent. A single yellow band was eluted that was concentrated and cooled to 0° to yield $(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)H$ (0.32 g, 48%), identified by comparison to an authentic sample.[12,13]

$(\eta^5$-Cyclopentadienyl)carbonyl(cyanomethyl)(triphenylphosphine)iron(II) (2). A solution of *ca.* 20 mmol of $LiCH_2CN$ in THF (500 ml) at −78° was prepared by the method of Crouse and See-

Page 663. The first 18 lines on this page duplicate the last 18 lines on page 662 and should be deleted.—D. L. Reger

Itamar Bodek, Geoffrey Davies,* and John H. Ferguson: Studies of Ammineaquocobalt(III) Chemistry. Kinetics and Mechanisms of Formation and Dissociation of Monochlorodiammineaquocobalt(III) Complexes and of the Reduction of *cis*-Diammineaquocobalt(III) Species by Br^- in Acid Perchlorate Solution.

Page 1709. In column 1, the first sentence of the paragraph on High-Temperature Synthesis should begin: "An ice-cold solution of $CoCl_2 \cdot 6H_2O$ (20 g, 0.084 mol) and H_2O_2 (5 ml, 10 M, 0.05 mol) in 50 ml of water.....". Later in the same sentence the values in parentheses after $KHCO_3$ should be 40 g, 0.4 mol.—Itamar Bodek