$$[\pi\text{-}C_5H_5Fe(CO)_2]_2SnCl_2 \;+\; 2C_6H_5SH \;\xrightarrow[-2(C_2H_5)_3NHCl]{2(C_2H_5)_3N}\; [\pi\text{-}C_5H_5Fe(CO)_2]_2Sn(C_6H_5)_2$$

<div align="center">II</div>

$$[\pi\text{-}C_5H_5Fe(CO)_2]_2SnCl_2 \;+\; \begin{array}{c} H_2C\!-\!SH \\ | \\ H_2C\!-\!SH \end{array} \;\xrightarrow[-2(C_2H_5)_3NHCl]{2(C_2H_5)_3N}\; [\pi\text{-}C_5H_5Fe(CO)_2]_2Sn\!\!\begin{array}{c} S\!-\!CH_2 \\ | \\ S\!-\!CH_2 \end{array}$$

<div align="center">III</div>

<div align="center">IV</div>

The complexes II–IV appear to be stable in air both in the crystalline state and in solution in organic solvents, although all, especially III, are somewhat sensitive to light.

Very recently similar reactions between ethane-1,2-dithiol and $Cl_2Sn[M(CO)_5]_2$ (where M = Mn, Re) to give tin–sulfur heterocycles have been reported.[3]

Treatment of I with potassium thiocyanate in acetone yields the light-sensitive complex $[\pi\text{-}C_5H_5Fe(CO)_2]_2Sn(NCS)_2$ (V). The infrared spectrum of this compound provides no conclusive evidence for its formulation as an isothiocyanate, as in the regions where characteristic frequencies of the –NCS group fall [2080–2010 cm^{-1} (–C=N str) and 860–780 cm^{-1} (C—S str)][4,5] carbonyl and π-cyclopentadienyl ring vibrations, respectively, also occur. However the absence of absorption in the region of the spectrum characteristic of S-bonded thiocyanate [690–720 cm^{-1} (C—S str)][5] and the fact that the NCS group usually bonds to tin through nitrogen[6] may suggest that the formulation of V as an isothiocyanate is correct.

Experimental Section

All reactions were carried out under an atmosphere of dry nitrogen. Dichlorobis(dicarbonyl-π-cyclopentadienyliron)tin was prepared by a standard method.[7] Microanalyses were performed by Alfred Bernhardt Mikroanalytisches Laboratorium, Mülheim, Germany.

Bis(dicarbonyl-π-cyclopentadienyl)bis(phenylthio)tin (II).—A solution of thiophenol (1.1 g, 10 mmol) and triethylamine (1.0 g, 10 mmol) in benzene (50 ml) was added dropwise with stirring to $[\pi\text{-}C_5H_5Fe(CO)_2]_2SnCl_2$ (2.72 g, 5 mmol) in benzene (50 ml). Immediate precipitation of triethylamine hydrochloride occurred, and the solution turned deep red. The reaction mixture was stirred at room temperature (2 hr), when triethylamine hydrochloride (1.20 g, 94%; mp 250–252°, lit.[8] 254°) was filtered off. Removal of solvent from the filtrate gave a brown oil from which ochre crystals of the product were isolated by dissolving in acetone and precipitating with water; yield 2.90 g (84%); mp 132–134°. *Anal.* Calcd for $C_{26}H_{20}Fe_2O_4S_2Sn$: C, 45.2; H, 2.92; S, 9.3. Found: C, 45.3; H, 2.99; S, 9.1. Infrared spectrum in chloroform: ν_{CO}: 2017 vs, 1994 vs, 1961 s cm^{-1}.

2,2-Bis(dicarbonyl-π-cyclopentadienyliron)-2-stanna-1-3-dithiacyclopentane (III) was prepared similarly. After removal of triethylamine hydrochloride, the filtrate was evaporated to small bulk and petroleum ether (bp 40–60°) was added to precipitate the product, which was obtained as orange-yellow microcrystals (60%); mp 160–160–165° after two recrystallizations from aqueous methanol. *Anal.* Calcd for $C_{16}H_{14}Fe_2O_4S_2Sn$: C, 34.0; H, 2.50; S, 11.4. Found: C, 34.2; H, 2.55; S, 11.2. Infrared spectrum in chloroform: ν_{CO}: 2011 s, 1990 vs, 1965 s cm^{-1}; in cyclohexane: 2015 s, 1997 s, 1991 vs, 1963 s, 1951 s cm^{-1}.

The crude product IV was recrystallized from chloroform–methanol to afford deep orange plates (72%), mp 172–173°. *Anal.* Calcd for $C_{21}H_{16}Fe_2O_4S_2Sn$: C, 40.2; H, 2.57; S, 10.2; Sn, 18.9. Found: C, 40.0; H, 2.46; S, 10.4; Sn, 19.1. Infrared spectrum in chloroform: ν_{CO}: 2018 vs, 1993 s, 1962 s, 1950 sh cm^{-1}; in cyclohexane: 2020 vs, 1990 s, 1968 s, 1950 m cm^{-1}.

Diisothiocyanatobis(dicarbonyl-π-cyclopentadienyliron)tin. (V).—$[\pi\text{-}C_5H_5Fe(CO)_2]_2SnCl_2$ (1.37 g, 2.5 mmol) and potassium thiocyanate (0.8 g, 8.1 mmol) were heated under reflux in acetone (50 ml) for 2 hr. Potassium chloride (0.29 g, 80%) was filtered off and water (100 ml) was added to the filtrate, when the crude product (1.15 g, 77%) separated. It was twice recrystallized from chloroform–methanol to give orange, light-sensitive needles, mp 197° dec. *Anal.* Calcd for $C_{16}H_{10}Fe_2N_2O_4S_2Sn$: C, 32.6; H, 1.71; Fe, 19.0; S, 10.9. Found: C, 32.6; H, 1.69; Fe, 19.0; S, 11.4. Infrared spectrum in chloroform (broad poorly resolved bands): ν_{CO} and ν_{CN}: 2025 vs, 2008 vs, 1985 s, 1965 sh cm^{-1}.

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Lanthanide Picolinate Chelate Stabilities[1]

BY J. E. POWELL AND J. W. INGEMANSON

Critical examination of the stability data for lanthanide picolinates reported by Thompson[2] reveals that K_1/K_2 ratios do not coincide with the ratios observed when α-hydroxyisobutyrate and 1-hydroxycyclopentane-1-carboxylate (HCPC) anions bond bidentately to tripositive lanthanide cations[3,4] and that K_2/K_3 ratios are inordinately small in view of the theories of Bjerrum.[5] Previous work by Powell, *et al.*,[4]

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shows (in media of ionic strength 0.1) that K_1/K_2 and K_2/K_3 ratios either equal or exceed the ratios computed on a purely statistical basis in agreement with the proposition[5,6] that $*K_{n-1}/*K_n = *P = SRT$ ($*P$ being the observed ratio of thermodynamic constants, S being a statistically derived value, and R and T being additional steric and electrostatic factors, respectively).

What is not commonly appreciated is that the purely statistical contribution S is applicable to cases of both symmetrical and unsymmetrical ligands, whether neutral or charged. Exclusion or repression of certain bonding modes due to steric considerations does contribute to $*K_{n-1}/*K_n$ ratios, but through R (the so-called "rest" factor) rather than S. It is clearly redundant to consider either steric or electrostatic factors in evaluating S in view of the fact that the above expression for $*K_{n-1}/*K_n$ includes both an electrostatic term T and a catch-all correction factor R (defined by Bjerrum as a "rest" or "everything else" factor). It is our contention, therefore, that the term R should include all contributions related to ligand asymmetry and to steric effects.

It should be pointed out that Bjerrum's theory regarding P values is valid only for ratios of true thermodynamic step formation constants. At ionic strengths other than zero

$$P = K_{n-1}/K_n = (*K_{n-1}/*K_n)f(\mu) = \\ *Pf(\mu) = SRTf(\mu) \quad (1)$$

It is merely fortuitous then that the stepwise formation constant ratios observed at 0.1 ionic strength with lanthanide α-HIB and HCPC chelates nearly coincide with purely statistical contributions predicted by the models of Powell and Rowlands.[4] The coincidence arises apparently from the fact that $f(0.1)$ just happens to equal *ca.* $1/T$ (at least in the case of K_1/K_2).[3,6,7]

It is difficult to imagine any factor involved in the formation of successive lanthanide picolinate species that should cause either R or T to assume a value less than unity. Clearly, the value of R ought to increase as the complexity and bulk of the cation (as well as the ligand) increase, and T ought to increase as the effective charge of the complex cation decreases owing to successive attachment of oppositely charged ligand species. Consequently, rare earth picolinate K_2/K_3 ratios are to be expected to exceed a minimum value of 3.06 (the value of S computed solely on the basis of a bidentate ligand bonding to a presumably nine-coordinate cation, ignoring additional effects which arise owing to ligand asymmetry or to charge considerations). Since Thompson[2] has reported K_2/K_3 values as low as 0.8, it is clear that errors are involved and that the system needs to be reconsidered.

Experimental Section

Picolinic Acid–Picolinate Buffer.—Reagent grade 2-picolinic acid was obtained from K & K Laboratories and further purified by sublimation at reduced pressure (2–3 mm). The sublimate

(mp 135.2–136.4° (uncor), lit. mp 137°;[8] apparent purity 99.1%, by acidimetry) was used to prepare a stock of buffer solution (0.1010 N in HL and 0.0950 N in KL).

Ionization Constant of the Acid.—A series of 20 individual dilutions of the buffer (all adjusted to 0.100 M ionic strength by appropriate additions of KNO_3) was prepared. The volumetric flasks of diluted buffer were carefully equilibrated in a 25.0° water bath; and the pH_o of each individual dilution was read to a precision of 0.0002 unit, using the Beckman Research pH meter, Model 1019, standardized *vs.* known concentrations of mineral acid (likewise at $\mu = 0.100$ (KNO_3)). K_a was determined as a slightly variable linear function of the picolinate anion concentration by means of a least-squares program devised in this laboratory. The variable ionization parameter at 25.0°, $\mu = 0.100$ (KNO_3), was found to be $K_a = (6.20 - 1.22[L^-]) \times 10^{-6}$ up to $[L^-] = 0.03 M$.

Stability Constant Determinations.—In the case of each rare earth, a similar series of 25 dilutions of picolinate buffer was prepared in 100-ml volumetric flasks to which 2.00 ml of 0.100 M rare earth nitrate and appropriate varying amounts of standard KNO_3 had been introduced. The resulting solutions were all at ionic strength 0.100 (after diluting to volume) and 0.002 M in total rare earth, but they contained varying known amounts of picolinate–picolinic acid buffer. After equilibrating at 25.0°, the pH_c of each solution was read to 0.0002 unit (although the reproducibility of the machine is probably no better than 0.001 unit). The β_n values and individual stepwise formation constants K_n were computed on the 360/50 IBM computer, using a four-parameter least-squares program adapted in this laboratory from the work of Sullivan, *et al.*,[9] and Rydberg.[10] The adapted program selects a more appropriate K_a value in each successive iteration using the previous $[L^-]$ value for each of the 25 data points and utilizes the new set of K_a values in computing the next generation of β_n values, until the new values of β_1, β_2, β_3, and β_4 differ individually by less than 1 part in 1000 from the previous ones. The step formation constants, K_1, K_2, K_3, and K_4, computed from the final β_n values, are recorded in Table I

TABLE I

STEP FORMATION CONSTANTS FOR THE RARE EARTH PICOLINATE CHELATE SPECIES AT 25° AND $\mu = 0.100$ (KNO_3)

Rare earth	n_{max}	$10^{-3}K_1$	$10^{-3}K_2$	$10^{-2}K_3$	10^{-2} K_4	K_1/K_2	K_2/K_3
La	2.6	3.2(3.5)a	0.9(0.5)a	1.9(4)a	0.2	3.8(6.3)a	4.4(1.2)a
Ce	2.8	4.9(5.5)	1.4(0.7)	3.3(9)	0.4	3.6(8.3)	4.3(0.8)
Pr	3.3	6.7(7.1)	2.0(1.3)	4.5(9)	1.0	3.4(5.5)	4.4(1.4)
Nd	3.2	7.6(7.6)	2.3(1.1)	5.5(12)	1.1	3.3(6.9)	5.1(0.9)
Pm	...	...	...	...	...	...	...
Sm	3.4	9.4(11.5)	2.9(2.2)	6.8(16)	1.6	3.2(5.3)	4.3(1.4)
Eu	3.3	9.8(11.8)	2.9(2.6)	7.2(13)	1.5	3.4(4.6)	4.0(2.0)
Gd	2.7	9.6(11.5)	2.7(1.9)	6.7(14)	1.8	3.6(6.0)	4.0(1.4)
Tb	3.3	12.0(14.2)	3.0(3.0)	5.7(10)	1.5	4.0(4.8)	5.3(3.0)
Dy	3.2	14.5(16.6)	3.5(3.5)	5.5(11)	1.3	4.2(4.8)	6.4(3.2)
Ho	3.1	15.5(16.6)	3.8(3.2)	5.7(10)	0.9	4.1(5.2)	6.7 3.2
Er	3.2	18.1(19.1)	4.8(3.8)	6.9(11)	1.2	3.8(5.0)	7.0(3.5)
Tm	3.2	21.4(23.0)	5.6(4.2)	7.4(17)	1.1	3.8(5.5)	7.5(2.5)
Yb	3.3	25.0(27.0)	6.8(4.9)	8.9(15)	1.3	3.7(5.5)	7.6(3.3)
Lu	3.4	26.0(28.2)	7.3(5.6)	9.6(16)	1.7	3.6(5.0)	7.6(3.5)

^{a} Values in parentheses were computed from data of Thompson.[2]

along with K_1/K_2 and K_2/K_3 ratios. The data of Thompson[2] are given in parentheses for comparison. Attention is called to the fact that $\bar{n}$ values exceeding 3.0 were observed in our experiments, necessitating the inclusion of a parameter β_4 in our computations. While the K_4 values recorded in Table I may be in error by as much as $\pm 50\%$, there is no uncertainty regarding the presence of a 1:4 rare earth picolinate species. It is estimated that the other three stability constants, K_1, K_2, and K_3, are accurate to ± 2, ± 4, and $\pm 8\%$, respectively. Part of the uncertainty in each case is related to the fact that (as in the case

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of the K_a evaluation) activity coefficients vary to a degree in each set of multicomponent systems, even though extraordinary care is taken to maintain the ionic strength of the media at 0.100.

Conclusions

The current results are more acceptable from a theoretical viewpoint than the earlier data. In particular, the K_1 and K_3 values are lower and the K_2 values are higher than those reported by Thompson;[2] thus the new K_1/K_2 ratios are smaller and the K_2/K_3 values are larger than those obtained from data reported previously, while both sets of ratios show improved internal consistency. The new average K_1/K_2 value (3.7 ± 0.3) is definitely less than the S_{12} value (4.92) required in the case of tridentate ligandcy but greater than the S_{12} value (3.27) required for bidentate ligandcy. The K_2/K_3 ratios also satisfy the requirements for bidentate bonding of the ligand to a nine-coordinate cation; *i.e.*, in general, $K_2/K_3 > S_{23} = 3.06$. The rising trend of K_2/K_3 noted with the heavier rare earths is consistent with the mounting steric hindrance expected when several bulky ligand anions are grouped about cations of smaller and smaller dimensions.

It is seen that the new data, particularly the $\bar{n}$ values exceeding 3.0, confirm the contention of Thompson[2] that the 2-picolinate anion functions bidentately in bonding to lanthanide cations. Monodentate behavior can be discounted in view of the large magnitudes of the step formation constants. Our data in no way discredit the likelihood that the coordination number of the lighter elements of the series (La^{3+}–Nd^{3+}) may be 10 rather than 9. Data of Spedding, *et al.*,[11–14] demonstrate rather conclusively that the lighter rare earth cations in dilute aqueous media are more highly hydrated than the smaller, heavier ones.

The data confirm, in a general way, the hypothesis of Devine[3] that the activity coefficient correction for K_1/K_2 at 0.1 *M* ionic strength tends to cancel the electrostatic term T of Bjerrum[5] which has been estimated by Manning[6] to have a value of about 1.5 when K_1 and K_2 are the successive step formation constants of the LnL^{2+} and LnL_2^+ species. A value of $T \simeq 1.5$ is certainly reasonable in view of the fact that an L^- species closely interacting with an Ln^{3+} species should tend to reduce the effective attracting charge from $3+$ to $2+$. The deviations of K_1/K_2 and K_2/K_3 from S_{12} and S_{23} are attributable, most likely, to steric hindrance, arising from the bulk and relative inflexibility of the picolinate anion. Recent work by Matkovich[7] in this laboratory has shown, in the case of the α-hydroxyisobutyrate anion, that $*K_1/*K_2 \simeq 1.5S_{12}$ with both neodymium (to which α-HIB[3] and HCPC[4] attach tridentately) and thulium (to which α-HIB[3] and HCPC[4] bond bidentately) at ionic strength 0. The work of Matkovich[7] supports the magnitude of the electrostatic factor es-

timated by Manning[6] and the hypothesis by Devine[3] that this electrostatic term is largely negated by a compensating ionic strength factor in 0.1 *M* media.

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The Metallic Nature of Osmium Dioxide

BY J. E. GREEDAN,[1a] D. B. WILLSON,[1b] AND T. E. HAAS

The temperature-independent paramagnetic susceptibility of OsO_2, $\chi_M = 119 \times 10^{-6}$ cgsu in the range 77–500°K, is atypically low for Os(IV) compounds[2] and suggests that it may be best not to consider this material as an ordinary coordination compound. In order to characterize OsO_2 and to investigate its electronic structure we undertook to grow single crystals of this material and to make electrical-transport measurements on these crystals.

Experimental Section

Crystal Growth.—Single crystals of osmium dioxide were grown by chemical transport using osmium tetroxide as the transporting agent under conditions similar to those described by Schäfer[3] with modifications in procedure adapted from the transport of WSe_2 and $NbSe_2$ as described by Kershaw, Vlasse, and Wold.[4] Osmium metal was prepared by the reduction of hydrated osmium dioxide in a stream of hydrogen at 400–500°. OsO_4 was used as received from Alfa Inorganics, Inc. Osmium metal (0.60 g, 0.0032 g-atom) and OsO_4 (0.85 g, 0.0033 mol) were placed in a Vycor tube of 10-mm i.d. which had been sealed off at one end. The tube was frozen, evacuated, and filled with oxygen. This operation was repeated four times. The Vycor tube was then sealed off to a length of 20 cm and placed in the crystal-growing furnace.

Crystal growth was carried out in a two-zone furnace. The zone temperatures were maintained by separate heaters. An 11-cm length of the tube rested in the reaction or hot zone and 9 cm rested in the cold or growth zone. At the start of the experiment the growth zone temperature was raised to 960° while the reaction zone was kept at about 250°. The reaction zone temperature was then raised to 960°, while the growth zone was held at the same temperature. Finally, the growth zone temperature was lowered at a rate of 1–5°/hr to 900°. These transport conditions were maintained for 7 days.

About 12 crystals of a coppery metallic luster were recovered, most of them in the form of elongated rectangular parallelepipeds. The crystals ranged in size from about 7 × 5 × 3 mm to those only a few tenths of 1 mm on a side. Three larger crystals were especially well formed, and these were chosen for electrical-transport experiments. A typical size for these crystals was about 5 × 2 × 1 mm.

OsO_2 crystals were analyzed by hydrogen reduction at 350–380°. *Anal.* Calcd: Os, 85.6. Found: Os, 85.5.

The density of OsO_2 was calculated from the unit cell param-

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