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The Affinity of Mercury(II) for Cobalt(III)-Bound Thiocyanate Ion

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The equilibrium constants for reaction between Hg^{2+} and NCS^- bound to $Co(III)$ have been measured for several $Co(III)$ complexes. Formations of both $L_5CoNCSHg^{n+}$ and $(L_5CoNCS)_2Hg^{m+}$ are important. At 25° and at ionic strength and $[H^+] = 0.1$ M, the values of these equilibrium constants, $K_1 = [L_5CoNCSHg^{n+}][Hg^{2+}]^{-1}[L_5CoNCS^{(n-2)+}]^{-1}$ and $K_2 = [(L_5CoNCS)_2Hg^{m+}][L_5CoNCSHg^{n+}]^{-1}[L_5CoNCS^{(n-2)+}]^{-1}$, are as follows: for $Co(NH_3)_5NCS^{2+}$, $K_1 = 9.8 \times 10^4$ M^{-1}, $K_2 = 1.4 \times 10^4$ M^{-1}; for *trans*-$Co(en)_2ClNCS^+$, $K_1 = 1.35 \times 10^5$ M^{-1}, $K_2 = 1.5 \times 10^4$ M^{-1}; for *trans*-$Co(en)_2H_2ONCS^{2+}$, $K_1 = 2.3 \times 10^4$ M^{-1}, $K_2 = 2.6 \times 10^3$ M^{-1}; for *cis*-$Co(en)_2NO_2NCS^+$, $K_1 = 6.9 \times 10^5$ M^{-1}, $K_2 = 5.3 \times 10^4$ M^{-1}. These data are utilized to analyze Hg^{2+}-induced aquations and to probe the role of binuclear complex formation in inner-sphere electron-transfer reactions.

The aquation of various halide ion containing complex ions in the presence of Hg^{2+} has been studied to gain information about the effect of ionic strength on kinetic parameters[1] and the catalytic effect on ionic reactions by polyelectrolytes,[2] to provide models for inner-sphere electron-transfer reactions,[3-6] to generate "five-coordinated" intermediates,[7] and to serve as a probe into the nature of spontaneous aquations.[5] A common feature of most of these studies is the reasonable assumption that a binuclear species involving a sharing of the halide ion ligand between the complex ion and Hg^{2+} exists. Our interest in reactions between Hg^{2+} and L_5CoNCS^{n+} species is an outgrowth of concern about the range of stabilities of these binuclear complexes as the other ligands of the $Co(III)$ center are changed. In the earlier study[5] of the reaction

$$L_5CoCl^{n+} + Hg^{2+} = L_5Co(OH_2)^{(n+1)+} + HgCl^+ \qquad (1)$$
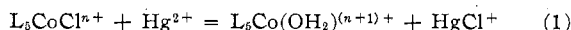
it was shown that a rough linear free energy relationship between the rates of reaction 1 and of the corresponding spontaneous aquations exists. One assumption of this earlier work was that the rate constants presented measured the relative leaving ability of Cl^- and $HgCl^+$. This assumption requires that the stabilities of the binuclear species do not vary significantly as L_5 is changed.

The reaction between Hg^{2+} and L_5CoNCS^{n+}

$$Hg^{2+} + L_5CoNCS^{n+} = L_5CoNCSHg^{(2+n)+} \qquad (2)$$

offers a means of testing this assumption.

Yet another reason for determining data for reactions such as (2) concerns the recent interest in "precursor" complexes in discussions of electron-transfer reactions.[8-11] Whereas the existence of these complexes in inner-sphere reactions seems certain, it is not clear as yet how they influence the rate of reaction—a process that is determined only by the difference in free energy between the ground state and the transition state. Nevertheless, any knowledge to be gained concerning models for "precursor" complexes is useful; our measurements contribute to this knowledge by giving an indication of the type of variation in "precursor" stability to be expected as the nonbridging ligands are varied.

Experimental Section

Materials.—$[Co(NH_3)_5NCS](ClO_4)_2$ was prepared by treating $[Co(NH_3)_5H_2O](ClO_4)_3$ with NaCNS; the complex was recrystallized from dilute $HClO_4$. The other complexes used were prepared from *trans*-$[Co(en)_2Cl_2]Cl$. The *trans*-$[Co(en)_2Cl_2]Cl$ was not prepared by the usual literature procedure[12] but in a manner that increases the overall yield. $[Co(en)_2(NO_2)_2]Cl$ was prepared by a modification of the literature method.[13] A solution (total volume about 300 ml) of 0.8 mol of ethylenedi-

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(1) A. R. Olson and T. R. Simonson, *J. Chem. Phys.*, **17**, 1167 (1949).
(2) H. Morawetz and B. Vogel, *J. Amer. Chem. Soc.*, **91**, 563 (1969), and references therein.
(3) J. P. Candlin and J. Halpern, *Inorg. Chem.*, **4**, 1086 (1965).
(4) J. H. Espenson and S. R. Hubbard, *ibid.*, **5**, 686 (1966).
(5) C. Bifano and R. G. Linck, *ibid.*, **7**, 908 (1968).
(6) J. P. Birk, *ibid.*, **9**, 735 (1970).
(7) See, for example, D. A. Buckingham, I. I. Olsen, and A. M. Sargeson, *ibid.*, **6**, 1807 (1967); D. A. Loeliger and H. Taube, *ibid.*, **5**, 1376 (1966); G. E. Dolbear and H. Taube, *ibid.*, **6**, 60 (1967).

(8) N. Sutin, *Accounts Chem. Res.*, **1**, 225 (1968).
(9) H. Taube and E. S. Gould, *ibid.*, **2**, 321 (1969).
(10) R. C. Patel, R. E. Ball, J. F. Endicott, and R. G. Hughes, *Inorg. Chem.*, **9**, 23 (1970).
(11) See also D. J. Barclay, E. Passeron, and F. C. Anson, *ibid.*, **9**, 1024 (1970), and references therein.
(12) J. C. Bailar, Jr., *Inorg. Syn.*, **2**, 222 (1946).
(13) H. F. Holtzclaw, Jr., D. P. Scheetz, and B. D. McCarty, *ibid.*, **4**, 176 (1953).

TABLE I
ANALYTICAL DATA FOR Co(III)–NCS COMPLEXES

Complex	Absorption spectrum, λ $(\epsilon)^a$ Lit.	Found	Anal, % Calcd	Found
[Co(NH₃)₅NCS](ClO₄)₂	4970 (177.4)[15]	4970 (175.5)^b		
	3050 (1550)[15]	3050 (1550)^b		
trans-[Co(en)₂ClNCS]ClO₄	5570 (132)[16]	5600 (138)^b		
		3040 (1980)^b		
trans-[Co(en)₂H₂ONCS](NO₃)₂·H₂O	5800 (100.3)[17]	5800 (105)	14.85 (Co)	15.13 (Co)
		5370 (187)^b		
	5310 (185.1)[17]	5310 (183)		
	4900 (99.6)[17]	4900 (90.7)		
	4600 (57.7)[17]	4600 (53.3)		
		3290 (1480)^b		
cis-[Co(en)₂NO₂NCS]₂SO₄		4750 (297)^b	17.80 (Co)	17.34 (Co)
		3230 (3045)^b	25.38 (N)	25.01 (N)
			18.13 (C)	17.84 (C)
			4.83 (H)	4.77 (H)

^{a} λ in Å; ϵ in l. mol⁻¹ cm⁻¹. ^{b} Absorption maximum.

amine was partially neutralized with concentrated HCl (0.48 mol), 0.4 mol of CoCl₂·6H₂O and 1.23 mol of NaNO₂ were added, and the resultant solution was aerated. The resulting yellow precipitate was filtered, washed with ethanol and ether, and dried at 50°; yield, 85.5% Co(en)₂(NO₂)₂Cl based on CoCl₂·6H₂O. Treatment of the Co(en)₂(NO₂)₂⁺ ion with concentrated HCl at 50–60° led to evolution of HNO₂ and to precipitation of a solid containing a mixture of *cis*- and *trans*-Co(en)₂Cl₂⁺ ions. This solid was dissolved in warm concentrated HCl and heated until the color became green. The solution was cooled and filtered; the green solid was dried at 110° for 2 hr to liberate the HCl of crystallization; total overall yield from CoCl₂·6H₂O, 70%.

The procedures used to prepare the other complexes from *trans*-Co(en)₂Cl₂⁺ are those described by Werner: *trans*-[Co(en)₂NCSCl]ClO₄,[14a] *trans*-[Co(en)₂H₂ONCS](NO₃)₂·H₂O,[14b] and *cis*-[Co(en)₂NO₂NCS]₂SO₄.[14c] Table I lists the data[15–17] relevant to establishing the purity of the complexes. Analysis for Co was done by reducing the complex to Co(II) with SnCl₂·2H₂O in HCl, evaporating to dryness, and dissolving the solid in concentrated HCl. The extinction coefficient ϵ is 560.7 ± 2.0 M^{-1} cm⁻¹.

Mercuric perchlorate solutions were prepared from mercuric nitrate that was repeatedly recrystallized as the oxide with Na₂CO₃ and redissolved with perchloric acid. The final solution was analyzed for Hg(II) by titration with NCS⁻[18] and by titration with EDTA.[19] The two analyses agreed to within 0.4%. The total [ClO₄⁻] in the Hg(II) solution was determined by ion-exchange techniques and the [H⁺] by titration of an aliquot of the Hg(II) solution treated with excess KNCS with standard NaOH. The value of [ClO₄⁻] and the sum 2{[Hg(II)] + [H⁺]} indicated the concentration of Na⁺ or other cations was very small. Perchloric acid solutions were made from Baker perchloric acid by dilution with doubly distilled water.

Technique.—Measurements were made spectrophotometrically on a Cary Model 14 spectrophotometer equipped with a thermostated cell block. Solutions of the appropriate Co(III) complex dissolved in 0.100 *N* HClO₄ were placed in a spectrophotometer cell; the Hg(ClO₄)₂ solution, also in 0.100 *N* HClO₄, was added from micropipets. Values for the total [Co(III)] and total [Hg(II)] were determined from the dilution factors.

Calculations were performed on the CDC 3600 computer of the UCSD Computer Center.

(14) (a) A. Werner, *Ann.*, **386**, 133 (1912); (b) *ibid.*, 158 (1912); (c) *ibid.*, 236 (1912).
(15) K. Schug, M. D. Gilmore, and L. A. Olson, *Inorg. Chem.*, **6**, 2180 (1967).
(16) P. Benson and A. Haim, *J. Amer. Chem. Soc.*, **87**, 3826 (1965).
(17) C. K. Ingold, R. S. Nyholm, and M. L. Tobe, *J. Chem. Soc.*, 1691 (1956).
(18) A. I. Vogel, "Quantitative Inorganic Analysis," Wiley, New York, N. Y., 1951, p 264.
(19) J. F. Coetzee in "Treatise on Analytical Chemistry," Part II, Vol. 3, I. M. Kolthoff and P. J. Elving, Ed., Interscience, New York, N. Y., 1961, p 308.

Results

General Observations.—When a solution of Co(NH₃)₅NCS²⁺ is added to a solution containing Hg²⁺, there are slight changes in the visible region of the spectrum, but dramatic changes take place in the near-uv region. At the peak (3060 Å), the extinction coefficient changes from 1550 M^{-1} cm⁻¹ to an apparent value of 130 M^{-1} cm⁻¹ (the latter value is obtained in a solution with total [Hg(II)] = 0.01 *M*). Similar observations have been recorded by Larsson.[20] What is especially relevant to the determination of the equilibrium constant defined by reaction 2

$$K_1 = \frac{[\text{Co}^{\text{III}}\text{NCSHg}^{\text{II}}]}{[\text{Hg}^{\text{II}}][\text{Co}^{\text{III}}\text{NCS}]}$$

is revealed by a more careful examination of the spectral behavior of solutions containing variable amounts of Hg(II) but normalized to equal [Co(NH₃)₅NCS²⁺]. Examination of spectral scans from 3500 to 2500 Å indicates the lack of an isosbestic point. Such a result is consistent with a continuous variation experiment at 10⁻³ *M* in Hg(II) and Co(III).[21] The most logical explanation of the failure to observe isosbestic behavior, consistent with the continuous variations experiment, is that the reaction

$$\text{Co}^{\text{III}}\text{NCSHg}^{\text{II}} + \text{Co}^{\text{III}}\text{NCS} = (\text{Co}^{\text{III}}\text{NCS})_2\text{Hg}^{\text{II}} \qquad (3)$$
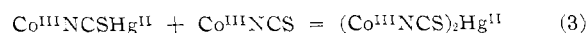
is important with

$$K_2 = \frac{[(\text{Co}^{\text{III}}\text{NCS})_2\text{Hg}^{\text{II}}]}{[\text{Co}^{\text{III}}\text{NCSHg}^{\text{II}}][\text{Co}^{\text{III}}\text{NCS}]}$$

Determination of Equilibrium Constants.—The system defined by reactions 2 and 3 cannot be solved analytically in closed form. There are four components in a solution—Hg²⁺, Co$^{\text{III}}$NCS, Co$^{\text{III}}$NCSHg$^{\text{II}}$, and (Co$^{\text{III}}$NCS)₂Hg$^{\text{II}}$; we shall denote the concentrations of these species by the symbols H, C, M, and D, respectively, and the compounds themselves by H, C, M, and D. In addition, there are three unknowns, K_1, K_2, and the extinction coefficient of D, ϵ_D. (We determine ϵ_M from experiments in which a large excess of Hg²⁺ is pres-

(20) R. Larsson, *Acta Chem. Scand.*, **16**, 931 (1962).
(21) W. C. Waggener, J. A. Mattern, and G. H. Cartledge, *J. Amer. Chem. Soc.*, **81**, 2958 (1959).

TABLE II

TYPICAL DATA FOR $Co(NH_3)_5NCS^{2+}$ + Hg(II)[a]

$10^5[Co(III)]$,[b] M	$10^5[Hg(II)]$,[b] M	Calcd[c]	Found
		Absorbance	
7.13	7.93	0.289	0.288
7.12	9.14	0.256	0.257
7.18	2.46	0.693	0.699
24.07	59.97	0.391	0.394
7.04	17.47	0.164	0.169
13.85	25.33	0.294	0.316
14.10	10.87	0.591	0.606
6.81	5.75	0.357	0.352
6.76	10.78	0.211	0.208
6.80	5.75	0.356	0.346
6.77	9.53	0.232	0.228
6.69	18.22	0.151	0.155
6.84	1.28	0.826	0.828

[a] These data are weighted by estimating that a 2% error exists in [Co(III)], a 1% error in [Hg(II)], a 2% error in the values for the extinction coefficients of C and M, and an error of 0.004 absorbance unit in the absorbance value. [b] Total concentrations of reagents. [c] Calculated from the parameters $K_1 = 9.88 \times 10^4$ M^{-1}, $K_2 = 1.47 \times 10^4$ M^{-1}, and ϵ_D 266.

ent so as to drive both C and D to M.) In order to obtain values for these unknowns, an iterative computer program was written. For guessed values of K_1 and K_2, an expression for C in terms of these constants and the

gus.[22]) This portion of the program uses Gauss's method to obtain linear equations. The only difficulty of note in this procedure is the lack of an analytical form for the necessary partial derivatives $\partial F_i/\partial K_1$ and $\partial F_i/\partial K_2$. These derivatives depend on having available analytical forms for $\partial C_i/\partial K_1$, etc. In the absence of such analytical forms, we have programmed the computer to approximate the value of these derivatives: $\partial C_i/\partial K_1 = \Delta C_i/\Delta K_1$ for small ΔK_1. Tests have shown that the choice of the size of the intervals ΔK_1 and ΔK_2 is such that the final answers are independent of that choice. The results are also relatively insensitive to the exact weights given the points.

In Table II we reproduce some of the data in order to illustrate the fit of observed and calculated absorbances. Table III gives the pertinent results obtained including the standard deviation of the parameters and the root-mean-square per cent deviation of the fit. The rather large standard deviations for K_1 and K_2 in the *cis*-Co-$(en)_2NO_2NCS^+$ system are a reflection of the small absorbance change in this case.

The only available data on Co(III) complexes with which to compare our results are those of Schug and coworkers. They reported[23] for $Co(NH_3)_5NCS^{2+}$ that $K_1 = 2.6 \times 10^5$ M^{-1} at 25° and ionic strength 0.16 M.

TABLE III

RESULTS OF LEAST-SQUARES ANALYSIS OF INTERACTION OF Hg(II) WITH $Co^{III}NCS$[a]

AT 25° AND IONIC STRENGTH = $[H^+]$ = 0.1 M

Complex	Fixed parameters	Range of total Hg(II), $M \times 10^{-5}$	Range of total Co(III), $M + 10^{-5}$	K_1, M^{-1}	K_2, M^{-1}	ϵ_D	Rms % dev
			λ 3060 Å				
$Co(NH_3)_5NCS^{2+}$ ($n = 29$[b])	ϵ_C 1550 ϵ_M 130	1.28–60.0	6.69–24.9	$(9.88 \pm 0.32) \times 10^4$	$(1.46 \pm 0.07) \times 10^4$	266 ± 26	2.15
			λ 3400 Å				
trans-$Co(en)_2ClNCS^+$ ($n = 26$[b])	ϵ_C 1650 ϵ_M 174	0.51–27.9	4.65–19.8	$(1.33 \pm 0.07) \times 10^5$	$(1.58 \pm 0.13) \times 10^4$	243 ± 56	1.73
			λ 3325 Å				
trans-$Co(en)_2H_2ONCS^{2+}$ ($n = 60$[b])	ϵ_C 1474 ϵ_M 159	0.36–178.6	3.22–109.5	$(2.21 \pm 0.07) \times 10^4$	$(2.52 \pm 0.32) \times 10^3$	267 ± 62	3.00
			λ 3050 Å				
cis-$Co(en)_2NO_2NCS^+$ ($n = 33$[b])	ϵ_C 2610 ϵ_M 1777	0.67–30.4	3.73–8.62	$(6.6 \pm 1.4) \times 10^5$	$(5.3 \pm 1.1) \times 10^4$	3713 ± 61	0.67

[a] The weighting of points is the same as described in footnote a of Table II; changing to equal weights or to increased percentage errors changes the values of K_1, K_2, and ϵ_D only within the standard deviations listed. [b] Number of separate data points.

total Hg(II) and total Co(III) in solution, T_H and T_{Co}, can be written. This cubic equation is solved by Newton's method for each datum point. The resultant concentrations of Co(III)NCS, C_i, are used to calculate M_i and D_i. These values, coupled with a guessed value of ϵ_D are then used to compute the calculated absorbance

$$F_i = l(\epsilon_C C_i + \epsilon_M M_i + \epsilon_D D_i)$$

where l is the length of the cell. The program then minimizes the sum of the squared deviations of the calculated and observed absorbances by means of a nonlinear least-squares procedure. (The points were weighted according to the procedure outlined by Hu-

This value is in satisfactory agreement with our value if consideration is given to the ionic strength difference. Their value of K_2 is less certain.[23b] A report on the affinity of Hg^{2+} for NCS^- bound to the $Cr(H_2O)_5^{3+}$ residue has also appeared.[24] This value is 1.6×10^4 M^{-1} at 25° and unit ionic strength. No mention is made of the complex $[(H_2O)_5CrNCS]_2Hg^{6+}$.

(22) Z. Z. Hugus, Jr., in "Advances in the Chemistry of the Coordination Compounds," S. Kirschner, Ed., Macmillan, New York, N. Y., 1961, p 379.
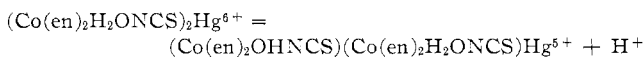
(23) (a) K. Schug and B. Miniatas, Abstracts, 155th National Meeting of the American Chemical Society, San Francisco, Calif., March 1968, No. M-136; (b) K. Schug, private communication.

(24) J. N. Armor and A. Haim, Abstracts, 156th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept 1968, No. INOR 55. A. Haim in a private communication, estimated K_2 in this case is about 10^2 M^{-1}.

Some qualitative observations we made during the course of this work warrant reporting. In all cases studied, a solution of Hg(II) and a Co^{III}NCS complex could be returned to an absorbance characteristic of the free Co(III) complex by treatment with excess HCl. These experiments demonstrate the reversibility of reactions 2 and 3. We have found that cis-Co(en)$_2$-ClNCS$^+$, in contrast to the trans isomer, is kinetically unstable in the presence of Hg^{2+} within the time required for the experiments, a fact previously reported by Tobe.[25] In addition, as might be expected by the labilizing power of a trans NO$_2^-$ group,[26] equilibrium studies on trans-Co(en)$_2$NO$_2$NCS$^+$ cannot be performed without extrapolations of the time-dependent absorbance to zero time. The spectral changes accompanying the formation of Co^{III}NCSHg^{II} complexes, M, can be determined by adding a large excess of Hg^{2+} to a solution of the complex. The values obtained are to be compared with those listed in Table I for the free Co^{III}-NCS complexes. They are as follows (complex, [Hg^{2+}], λ, Å (ϵ, M^{-1} cm^{-1})): Co(NH$_3$)$_5$NCS^{2+}, 0.10 M Hg(NO$_3$)$_2$, 4760, (89);[20] trans-Co(en)$_2$ClNCS$^+$, 2.2 × 10^{-2} M, 5420 (61), 4470 (32); trans-Co(en)$_2$H$_2$ONCS^{2+}, 4.2 × 10^{-2} M, 5120 (66), 4500 (sh) (47); cis-Co(en)$_2$-NO$_2$NCS$^+$, 2.2 × 10^{-2} M, 4530 (188), 3290 (2680). We find no evidence for an absorption maximum at 3330 Å in Co(NH$_3$)$_5$NCSHg^{4+} as claimed by Larsson.[20]

Discussion

The ratio of the equilibrium constants for reactions 2 and 3 is compared with ratios for other reactions of Hg^{2+} with halide, azide, and thiocyanate ions in Table IV.[27-30] The second ligand in the case of the halides and azide is only slightly less strongly bonded than the first. Even for a +2 charged ligand, Co(NH$_3$)$_5$NCS^{2+}, the relative affinities of Hg^{2+} for the first and second ligand differ by only a factor of 7. These values occur even though the charge on some of these complexes reaches +6. This result would appear to imply that the charge is distributed throughout the molecule in such a way that solvation of the highly charged complex does not inhibit its formation. Further support for this concept comes from qualitative experiments carried out at various acidities with the complex trans-Co(en)$_2$H$_2$O-NCS^{2+}. These experiments indicated no shift in either intensity or position of the absorbance of a mixture of this complex and Hg(II) over the acidity range 0.1–1.34 M in HClO$_4$. This result and the lower values for K_1 and K_2 for trans-Co(en)$_2$H$_2$ONCS^{2+} compared to the other complexes argue that acidic character of trans-Co(en)$_2$H$_2$ONCS^{2+} is *not* utilized in order to reduce net charge

$$\text{(Co(en)}_2\text{H}_2\text{ONCS)}_2\text{Hg}^{6+} =$$
$$\text{(Co(en)}_2\text{OHNCS)(Co(en)}_2\text{H}_2\text{ONCS)Hg}^{5+} + \text{H}^+$$

for if it were, one would expect this anomalous stability to show up in the apparent equilibrium constant measured at [H$^+$] = 0.1 M.

TABLE IV
EQUILIBRIUM CONSTANTS FOR REACTIONS OF Hg^{2+}

Ligand	$K_1,^a$ M^{-1}	$K_2,^b$ M^{-1}	K_1/K_2	Ref
NCS$^-$ ^{c}	2.7 × 10^{16} ^{h}			27
Co(NH$_3$)$_5$NCS^{2+} ^{d}	9.8 × 10^4	1.5 × 10^4	6.5	This work
trans-Co(en)$_2$ClNCS$^+$ ^{d}	1.31 × 10^5	1.6 × 10^4	8.2	This work
trans-Co(en)$_2$H$_2$ONCS^{2+} ^{d}	2.2 × 10^4	2.5 × 10^3	8.8	This work
cis-Co(en)$_2$NO$_2$NCS$^+$ ^{d}	6.6 × 10^5	5.3 × 10^4	12.4	This work
N$_3^-$ ^{e}	2.0 × 10^7	1.2 × 10^7	1.67	28
Cl$^-$ ^{f}	5.25 × 10^6	3.2 × 10^6	1.65	29
Br$^-$ ^{g}	2.5 × 10^9	3.8 × 10^8	6.6	30

^{a} Refers to the equilibrium Hg^{2+} + L^{n+} = HgL$^{(n+2)+}$. ^{b} Refers to the equilibrium HgL$^{(n+2)+}$ + L^{n+} = HgL$_2^{(2n+2)+}$. ^{c} At ionic strength 0.2 M. ^{d} At ionic strength 0.10 M. ^{e} At ionic strength 0.15 M. ^{f} At ionic strength 1.0 M. ^{g} At ionic strength 3.0 M. ^{h} This is the overall equilibrium constant K_1K_2.

Another means of demonstrating the insensitivity to the buildup of charge is to compare the affinity of CH$_3$Hg$^+$ with that of Co(NH$_3$)$_5$NCSHg^{4-} for Co(NH$_3$)$_5$-NCS^{2+}. The value of the association constant for the former reaction is 1.5 × 10^3 M^{-1},[31] whereas the latter is 1.4 × 10^4 M^{-1}. Factors other than charge clearly determine the values for these equilibrium constants.

An item of general interest is the spectral behavior of the complexes with two Co(III) species bound to a Hg^{2+}. In all cases, the molar absorbances of these species are about twice that of the CoL$_5$NCSHg^{n+} complexes. Qualitative observations over the entire near-uv range confirm this spectral feature. There appears to be no extraordinary electronic coupling between the two Co(III) centers through Hg(II) orbitals that gives rise to a low-energy transition.

The Hg^{II}–Co^{III}NCS Systems as a Model.—The determination of the equilibrium constants for reaction 2 allow us to assess the importance of changes in "nonbridging"[32] ligands on this stability constant. Table V[33-36] summarizes our data and offers a comparison with similar data on the reaction

$$\text{L}_5\text{CoOH}^{n+} + \text{H}^+ = \text{L}_5\text{CoOH}_2^{(n+1)+} \quad (4)$$

It can be seen from this comparison that the response to a change in "nonbridging" ligands is qualitatively similar in the two systems. Since these two series differ drastically in the nature of the interaction (soft–soft for Hg^{2+} + CoL$_5$NCS^{n+} and hard–hard for H$^+$ + CoL$_5$-OH^{n+}),[37] it seems likely that the variation of ΔF as the nonbridging ligands are changed will be valid for a variety of interactions.

(25) Quoted in M. E. Baldwin and M. L. Tobe, *J. Chem. Soc.*, 4275 (1960).

(26) S. Asperger and C. K. Ingold, *ibid.*, 2862 (1956).

(27) N. Tanaka, K. Ebata, and T. Murayama, *Bull. Chem. Soc. Jap.*, **35**, 124 (1962). See also C. J. Nyman and G. S. Alberts, *Anal. Chem.*, **32**, 207 (1960).

(28) T. R. Musgrave and R. N. Keller, *Inorg. Chem.*, **4**, 1793 (1965).

(29) L. Ciavatta and M. Grimaldi, *J. Inorg. Nucl. Chem.*, **30**, 197 (1968), and references therein.

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TABLE V

THE AFFINITY OF BOUND LIGANDS FOR
EXTERNAL REAGENTS AT 25.0°

Complex (Co(III))	K_1, M^{-1}		Ref
	Hg^{2+} a	H^+ b	
$Co(NH_3)_5X$	9.9×10^4	1.7×10^6	33
trans-$Co(en)_2H_2OX$	2.2×10^4	1.4×10^4 c	34
cis-$Co(en)_2NO_2X$	6.6×10^5	2.0×10^6	35
trans-$Co(en)_2ClX$	1.3×10^5	1.3×10^6 d	36

a Refers to the equilibrium Hg^{2+} + CoL_5X^{n+} = $CoL_5XHg^{(n+2)+}$. b Refers to the equilibrium H^+ + CoL_5OH^{n+} = $CoL_5OH_2^{(n+1)+}$. c Corrected for statistical factor. d At 20°.

If it is assumed that changing the X group in CoL_5-X^{n+} does not affect the trends seen in Table V, then the data can be used to assess the importance of precursor complex formation on studies in which the variation is made remote from the reaction center, variations in "nonbridging" ligands. We consider here two selected examples of such application. (1) The rates of Hg^{2+}-assisted aquations of chloro complexes of Co(III) have been correlated with the rate of spontaneous aquation.[5] The underlying assumption in this correlation was that precursor complex stability varied only slightly as the "nonbridging" ligands were varied. The deviation of trans-$Co(en)_2H_2OCl^{2+}$ from the correlation noted is now reasonably explained on the basis of the instability of the complex trans-$Co(en)_2H_2OClHg^{4+}$ relative to the precursor complexes of the other chloro compounds. (2) The second area in which these results are of consequence is in the consideration of precursor complexes in inner-sphere electron-transfer reactions.[8-10] Our results imply that studies of nonbridging ligand effects in

inner-sphere electron-transfer processes need consider at most a 3 kcal mol^{-1} variation in precursor stability (for nonbridging ligands of the type studied herein). Hence models in such studies are not highly sensitive to variable precursor stabilities.

On the other hand, the data presented can usefully be compared with those in an earlier paper[5] to demonstrate that the formation constant of complexes of the type L_5CoXHg^{n+} are quite sensitive to the nature of X. From the lack of deviation of second-order kinetics in the reaction of Hg^{2+} with $Co(NH_3)_5Cl^{2+}$,[5] an upper limit of 10 M^{-1} can be placed on K for Hg^{2+} + $Co(NH_3)_5Cl^{2+}$ = $Co(NH_3)_5ClHg^{4+}$. This number is to be compared with 9.9×10^4 M^{-1} for the corresponding reaction with NCS^- as the bridging group. On the other hand, reference to Table V indicates it is unlikely that the equilibrium constants for Cl^- and NCS^- binding to Hg^{2+} differ by more than a factor of 10^2. Thus the relative interaction of Hg^{2+} with these two ligands is a sensitive function of whether the ligand is bound to Co(III) or not. Such variations are likely to make arguments about rate patterns based on the precursor complex as a starting point dangerous unless care is taken to establish these stabilities.

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The Formation of Chelated Sulfate by Reactions between Sulfur Dioxide and Oxygen in the Coordination Sphere of Iridium and Ruthenium Complexes
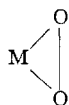
BY JOAN VALENTINE,[1] DONALD VALENTINE. JR.,[1] AND JAMES P. COLLMAN[*2]

Organo transition metal complexes containing bidentate sulfate may be prepared by adding SO_2 to MO_2 complexes or by adding O_2 to MSO_2 complexes. The scope of these reactions is discussed and new examples are reported for iridium, rhodium, and ruthenium complexes.

Introduction

Over the past few years several mononuclear diamagnetic oxygen complexes have been prepared through oxidative addition of O_2 to basic transition metal compounds.[3] Many of these complexes have been shown to have triangular

$$M \overset{O}{\underset{O}{\diagdown}}$$

structures in which the O–O bond distance is greatly increased in comparison with free O_2.[4]

A significant aspect of these complexes is the greater reactivity of coordinated oxygen toward reductants.[5] A broad class of oxygenases which occupy a central role in biology are metalloenzymes which apparently make use of metal-activated molecular oxygen.[6] The de-

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