Table II. Absorption Spectral Data for $LW(CO)_5$ in Hexane (MeOH), nm

L	$^1A_1 \rightarrow {}^3E^a$	$^1A_1 \rightarrow {}^1E^b$	$M \rightarrow L$ (CT)^c
Pyridazine	~430	394 (388)	437 (388)
Pyrazine	~430	398 (389)	416 (389)
Pyrimidine	~430	395 (380)	395 (339)

[a] ϵ ~500. [b] ϵ ~5000–7000. [c] ϵ ~5000–8000.

Table III. Electrochemical Data for $LW(CO)_5$,[a] V

L	E_{Ox}	E_{Red}
Pyridazine	1.04	2.56
Pyrazine	1.04	2.18
Pyrimidine	1.04	2.94

[a] 10^{-3} M CH_2Cl_2 + 0.01 M *tert*-butylammonium perchlorate.

complexes; therefore, to a large extent the relationship between the CT bands and the polarographic and theoretical data concerning the π^* orbitals of the diazines is fortuitous and certainly not a generalization that may be applied too widely. All three ligands subsequent to complexation remain bases by virtue of the "extra" nitrogen atom. These base strengths vary quite considerably, and, thus, the ability of various solvents to interact with the complexed ligands should also be a factor affecting the electronic structure of the metal complexes. Indeed, as Taube has shown, complexing the ligands to metallic π donors will increase such basicity for pyrazine, and excited CT states should be, and are, more basic than the ground states. Thus, solvation will play a very important, if at present unclear, role in such absorption spectral analysis. It is of interest that the order noted in hexane for the M–L CT band of $LW(CO)_5$ parallels the order of the $n \rightarrow \pi^*$ transition for the free ligands.[7]

We have attempted to use electrochemical analysis to shed further light upon the electronic structure of the complexes. Using cyclic-voltammetric techniques, we observed that the complexes undergo both one-electron oxidations and reductions but that all of these processes are nonreversible. However, the relative potentials at which these events take place lead to some interesting conclusions. The results of this study are collected in Table III.

All three complexes exhibit an oxidation potential under the conditions of the experiment at 1.04 ± 0.01 V. Since the electron removed in this process will come from the HOMO of the complex system, i.e., the $^1A_1$ metal-localized orbital configuration, this result confirms that variation of the ligands changes the ground-state electronic structure of the metal very little; i.e., as far as the metal is concerned, the primary feature of the complexes is that they are all N-bonded complexes; the ligand isomerization and varying base strengths seem of little account. The reduction potentials of the three complexes are very different, backing up the contention that the LUMO in the complex system if not totally ligand in character, certainly has a predominance of ligand character. The order of the reduction potentials is in the order predicted from theoretical considerations on the free ligands. Again, there is a discrepancy between the absorption data in hexane and the electrochemical data. When the absorption data are recorded under conditions identical with those of the electrochemical reduction experiment (CH_2Cl_2 with added tbap), the spectra are in most respects identical with those in methanol, and thus the discrepancy is not so startling since the CT band order is now pyrazine $\simeq$ pyridazine < pyrimidine.

Overall, the electrochemical study does reinforce the interpretation given to the absorption data above, i.e., a relatively constant-energy HOMO–metal-localized orbital system and a LUMO of considerable ligand character. It is interesting that the free ligands themselves are reversibly reduced to relatively stable anion radicals. That the complexes are not suggests that possible mixing of metal-localized antibonding and CT states occurs. (For the pyrimidine complex, since the CT band is much higher in energy than the LF band, it is possible that the reduction occurs directly into a metal-localized orbital.)

It is noteworthy that complexes of the type $[M(CO)_5(pyz)M(CO)_5]$ exhibit very low energy CT bands at $\simeq$600 nm and reversible electrochemical reduction, which we are currently investigating.

Acknowledgment. Support of this research was provided by the Robert A. Welch Foundation, Houston, Tex. We thank Dr. Keith Prater for the loan of cyclic voltammetric equipment and explanation and assistance on its use. Discussions with Dr. Lawrence Ellzey are also acknowledged.

Registry No. (pyridazine)$W(CO)_5$, 65761-20-8; (pyrazine)$W(CO)_5$, 65761-19-5; (pyrimidine)$W(CO)_5$, 65761-18-4.

References and Notes

(1) Portions of this paper have been presented at the Northwest Regional Meeting of the American Chemical Society, Portland, Ore., July 1977, and the XIIth Congreso Mexicano de Quimica Pura y Aplicada, Toluca, Mexico, Aug 1977. For Part 1 of this series see K. H. Pannell, C. Cheng-Yu Lee, C. Párkányi, and Richard Redfearn (nê snow), *Inorg. Chim. Acta*, **12**, 127 (1975)

(2) M. S. Wrighton, *Chem. Rev.*, **74**, 401 (1974).

(3) M. S. Wrighton, H. A. Abrahamson, and D. L. Morse, *J. Am. Chem. Soc.*, **98**, 4105 (1976).

(4) P. Ford, De F. P. Rudd, R. Gaunder, and H. Taube, *J. Am. Chem. Soc.*, **90**, 1187 (1968).

(5) M. S. Wrighton, G. S. Hammond, and H. Gray, *Mol. Photochem.*, **5**, 179 (1973).

(6) K. B. Wiberg and T. P. Lewis, *J. Am. Chem. Soc.*, **92**, 7154 (1970).

(7) F. Halverson and R. C. Hirt, *J. Chem. Phys.*, **19**, 711 (1951).

Correspondence

Ligand-Exchange Kinetics of (Ethylenediaminetetraacetato)lead(II) with (*R*)-(−)-1,2-Propylenediaminetetraacetic Acid

Sir:

In a recent publication[1] Pearson and co-workers have examined the ligand-exchange reaction kinetics of *R*(−)-PDTA with the lead complex of EDTA under a variety of pH conditions in 0.5 M KNO_3 ionic strength control. This communication presents an alternative mechanism for this exchange reaction at high pH. Although Pearson et al. have calculated a rate constant for the reaction of the tetraanion of PDTA with PbEDTA of 8.57 $M^{-1}\,s^{-1}$ at 20 °C in good agreement with our predicted value[2] for this system (12 $M^{-1}\,s^{-1}$ at 25 °C), two important points have been overlooked in their work.

The first such point is that the kinetics of these reactions show important dependencies upon the identity of the cation used in the "inert" buffers and ionic strength adjusting materials. Our work on closely related systems points this out and stability constants of these ligands with the alkali metal ions are available.[3-5] Potassium ion complexes a large fraction of the PDTA under these conditions and renders it considerably less reactive toward metal complexes, much in the same way that protonating the incoming ligand lowers its reactivity as observed by Pearson, ourselves, and other workers.[1,2,7] A

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Table I. Parameters Affecting Rate Constants of Hydroxide Accelerated Term[a]

pH	α_L^{4-} including K^+ complexation	α_L^{4-} excluding K^+ complexation	$10^4[OH^-]^2$	k_{obsd}, s^{-1}	$10^{-3}C_L$, M	$k_{obsd} - 8.57C_L\alpha$
10.041	0.0597	0.137	0.000056	0.0124	8.53	0.0024
10.569	0.117	0.349	0.000637	0.0303	8.55	0.0047
10.894	0.150	0.531	0.0028	0.0424	8.53	0.0036
11.001	0.158	0.592	0.0047	0.0498	8.52	0.0066
11.127	0.167	0.660	0.0083	0.0537	8.53	0.0054
11.449	0.182	0.802	0.0367	0.0623	8.52	0.0037
11.648	0.188	0.865	0.0917	0.0707	8.53	0.0075
11.756	0.191	0.892	0.151	0.0682	8.52	0.0031
11.869	0.192	0.915	0.254	0.0703	8.52	0.0035
11.998	0.194	0.935	0.459	0.0721	8.51	0.0039
12.036	0.194	0.940	0.547	0.0762	8.55	0.0073
12.102	0.195	0.948	0.742	0.0736	8.49	0.0046
12.137	0.195	0.952	0.871	0.0740	8.51	0.0046
12.145	0.195	0.953	0.904	0.0726	8.54	0.0028
12.176	0.195	0.956	1.04	0.0797	8.52	0.0099
12.290	0.196	0.966	1.76	0.0742	8.54	0.0035
12.356	0.196	0.971	2.39	0.0796	8.52	0.0087
12.384	0.196	0.973	2.72	0.0792	8.52	0.0082
12.405	0.197	0.974	2.99	0.0782	8.51	0.0072
12.421	0.197	0.975	3.22	0.0802	8.53	0.0089
12.435	0.197	0.976	3.44	0.0800	8.51	0.0088
12.437	0.197	0.976	3.47	0.0855	8.53	0.0141
12.462	0.197	0.976	3.89	0.0828	8.52	0.0115
12.497	0.197	0.978	4.57	0.0874	8.52	0.0160
12.565	0.197	0.981	6.25	0.0884	8.51	0.0168
12.601	0.197	0.983	7.38	0.0901	8.52	0.0183
12.627	0.198	0.984	8.32	0.0870	8.52	0.0151
12.655	0.198	0.985	9.47	0.0891	8.52	0.0172
12.663	0.198	0.985	9.82	0.0899	8.51	0.0181
12.705	0.198	0.986	11.92	0.0957	8.52	0.0237
12.725	0.198	0.987	13.07	0.104	8.52	0.0320
12.745	0.198	0.988	14.33	0.103	8.18	0.0338
12.802	0.198	0.989	18.63	0.114	8.51	0.0419
12.892	0.198	0.991	28.20	0.134	8.52	0.0616

[a] α_L (including K^+ complexation) is calculated by eq 7. α_L (excluding K^+ complexation) $= (1 + [H^+]/K_4)^{-1}$ where $pK_4 = 10.84$.

knowledge of the appropriate stability constants allows one to compute the rate constant of the truly "free" PDTA tetraanion.

The second point of concern is Pearson's interpretation of the high pH acceleration of the reaction as being due to greater reactivity of $Pb(OH)EDTA^{3-}$ and $Pb(OH)_2EDTA^{4-}$ compared to $PbEDTA^{2-}$. This implies that the high pH reaction is as in eq 1 and 2 with reaction 2 being rate determining.

$$PbY^{2-} + OH^- \overset{K_{OH}}{\rightleftharpoons} Pb(OH)Y^{3-} \qquad (1)$$

$$Pb(OH)Y^{3-} + L^{4-} \xrightarrow{k_3} PbL^{2-} + Y^{4-} + OH^- \qquad (2)$$

An alternative interpretation of such a rate enhancement at high pH is a hydroxide-catalyzed dissociation of the original complex followed by a rapid scavanging of the uncomplexed lead ion by $PDTA^{4-}$ such as is shown in eq 3 and 4.

$$PbY^{2-} + nOH^- \xrightarrow{k_{nOH}^{PbY}} PbOH_n^{(2-n)+} + Y^{4-} \qquad (3)$$

$$PbOH_n^{(2-n)+} + L^{4-} \xrightarrow{\text{fast}} PbL^{2-} + nOH^- \qquad (4)$$

A third possibility, that of a reaction sequence of eq 1 and 2 but with eq 2 being fast and eq 1 being rate limiting, cannot be differentiated from the second sequence by kinetic means. It would, however, be surprising if the replacement of an entire multidentate ligand would be fast compared to the formation of $Pb(OH)_nL$. That $Pb(OH)_nL$ cannot be observed in the absence of excess ligand also argues against this mechanism.

Either of these sequences would be occurring in parallel to the term which does not involve hydroxide ion which is shown in eq 5.

$$PbY^{2-} + L^{4-} \xrightarrow{k_1} PbL^{2-} + Y^{4-} \qquad (5)$$

In order to decide between these alternative pathways, the reaction must be studied at each of several widely different concentrations of PDTA while holding the reaction at each of several constant hydroxide ion concentrations. There is no evidence that this was done, the only statement made concerning PDTA concentration being "... reaction was made pseudo-first-order overall by using an approximate tenfold excess of the entering ligand." Analytical concentrations of PDTA for these reactions can be obtained by back-calculation of values listed in Table I of the work in question. Such values are included in Table I of this correspondence and are designated C_L. It is noted that $C_L = 8.52 \pm 0.03$ mM for all reactions except that at pH 12.745 for which $C_L = 8.18$ mM. In our earlier work on closely related systems,[2] we showed that the dissociative mechanism is a better explanation of the kinetic behavior than the enhanced reactivity of Pb(OH)Y. Unlike many other metal aminocarboxylate complexes, no mixed hydroxy complex has been detected by any of a variety of methods for lead(II) complexed to EDTA, PDTA, or CyDTA.[1,2,6,7] The data in Table I of the work under discussion can be interpreted as a dissociative hydroxide dependent reaction (eq 3 and 4) in parallel with eq 5. The calculations below presume a second-order dependence of the dissociative reaction on hydroxide ion as was shown for Pb–PDTA.[7] Equation 6 represents such a rate law.

$$\text{rate} = k_{obsd}[PbY]_T = k_L^{PbY}[PbY]C_L\alpha_L + k_{2OH}^{PbY}[PbY][OH^-]^2 \qquad (6)$$

$$\alpha = [PDTA^{4-}]/C_L = (1 + ([H^+]/K_4) + K_f[K^+])^{-1} \qquad (7)$$

$$k_{obsd} = k_L^{PbY}C_L\alpha_L + k_{2OH}^{PbY}[OH^-]^2 \qquad (8)$$

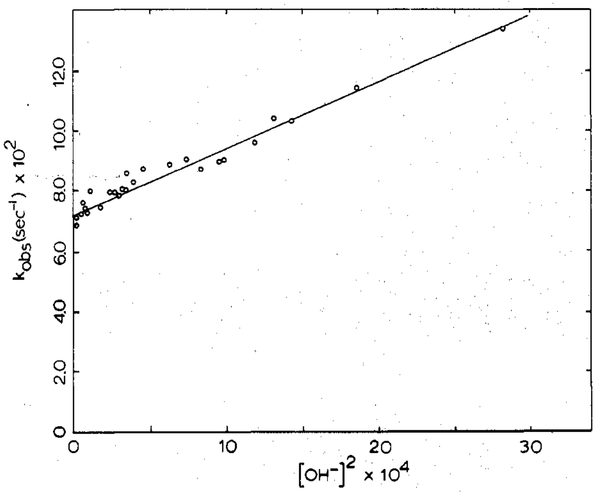

Figure 1. Plot of k_{obsd} vs. $[OH^-]^2$ for all data of pH >11.756. Above this pH, values of α_L are nearly constant. Intercept = $k_L^{PbY} = C_L = \alpha_L = 7.2 \times 10^{-}$ s^{-1}. Slope = k_{2OH}^{PbY} = 22.2 M^{-2} s^{-1}.

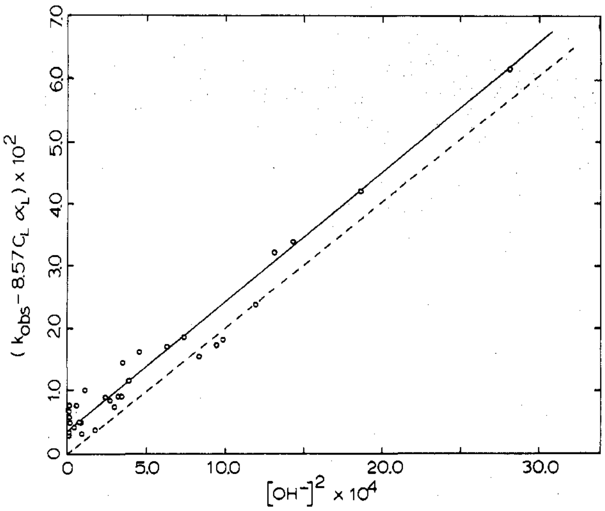

Figure 2. Plot of eq 8 rearranged with known values of k_L^{PbY}, C_L and α_L incorporated. The solid line uses k_L^{PbY} = 8.57 s^{-1} and has a slope = k_{2OH}^{PbY} = 20.7 M^{-2} s^{-1}. The dashed line is the line for a similar plot using k_L^{PbY} = 9.2 M^{-1} s^{-1}.

K_f is the formation constant for potassium ion complexation and equals $[KY^{3-}]/[K^+][Y^{4-}]$ = 8.06 at 25 °C.[3] K_4 is the fourth ionization constant of H_4PDTA in the absence of complexing ions such as potassium but in the presence of 0.5 M ionic strength controlled with a noncomplexing ion such as Cs^+ or $(CH_3)_4N^+$. pK_4 has been measured at 25 °C to be 11.01.[3] Based upon the ΔH of ionization of EDTA, pK_4 at 20 °C is estimated to be 11.11. The pK_w at 20 °C is taken to be 14.1669. Using these numbers, α can be calculated according to eq 7 and is included in Table I. Values of α as calculated by Pearson's method (eq 7 but without the $K_f[K^+]$ term) are also included in Table I and designated "$\alpha_{L^{4-}}$ excluding K^+ complexation".

Figure 1 is a plot of k_{obsd} vs. $[OH^-]^2$ in the region where α_L is effectively constant (pH >11.756; the range of values of α_L is 0.191–0.198). The linearity of this plot suggests that the second-order dissociative reaction is reasonable and has a rate constant of 22.2 M^{-2} s^{-1}. This value is approximately 20 times greater than the corresponding value for Pb–PDTA,[2] reflecting the greater stability constant of Pb–PDTA. The intercept of Figure 1 is measured to be 7.2×10^{-2} and is equal to $k_L^{PbY} C_L \alpha_S$. Using 8.52×10^{-3} as C_L, a value of k_L^{PbY} = 43.4 M^{-1} s^{-1} is calculated. This is in reasonable agreement with 30 M^{-1} s^{-1}, our earlier estimated value[2] of this rate constant in 0.5 M Cs^+ ionic medium.

Figure 2 is calculated utilizing pK_4 = 10.84 and ignoring K^+ complexation. In it, eq 8 is rearranged and known values of k_L^{PbY} = 8.57,[1] C_L, and α_L (Table I) are incorporated. The linearity of this plot demonstrates that eq 6 is sufficient to explain all the kinetic data presented in ref 1. The positive intercept can be eliminated by choosing k_L^{PbY} = 9.2 M^{-1} s^{-1} as is shown by the dashed line of Figure 2. The near-zero intercept of the dashed line implies that 9.2 M^{-1} s^{-1} is a better value of k_Y^{PbY} than is 8.57 M^{-1} s^{-1}.

Registry No. *R*(–)-PDTA, 15456-17-4; PbEDTA, 11112-42-8.

References and Notes

(1) S. J. Simon, J. A. Boslett, Jr., and K. H. Pearson, *Inorg. Chem.*, **16**, 1232 (1977).
(2) J. D. Carr and D. R. Baker, *Inorg. Chem.*, **10**, 2249 (1971).
(3) J. D. Carr and D. G. Swartzfager, *Anal. Chem.*, **43**, 583 (1971).
(4) J. D. Carr and D. G. Swartzfager, *Anal. Chem.*, **43**, 1520 (1971).
(5) J. D. Carr and D. G. Swartzfager, *J. Am. Chem., Soc.*, **95**, 3569 (1973).
(6) P. E. Reinbold and K. H. Pearson, *Inorg. Chem.*, **9**, 2325 (1970).
(7) J. D. Carr, K. Torrance, C. J. Cruz, and C. N. Reilley, *Anal. Chem.*, **39**, 1358 (1967).

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Received July 18, 1977

Is the Closo, Nido, or Arachno Classification for Boranes a Function of the Topological Description of the Molecule?

Sir:

Recently, Plesek, Hermanek, and Janousek[1] characterized the two interesting new heteroboranes 6,8-$S_2B_7H_9$ and 6,8-CSB_7H_{11} and also discussed the correct topological description of these molecules together with that of the isoelectronic 6,8-$C_2B_7H_{13}$ described earlier by Hawthorne.[2] It was pointed out that if a lone pair was considered to be equivalent to a substituent, the alternative topologies for these three molecules would be 2370 (corresponding to the isoelectronic $B_9H_{11}^{4-}$) and 2532 (corresponding to the isoelectronic $B_9H_{13}^{2-}$). Of particular concern were heteroatoms such as sulfur which exhibit "dual behavior" in that they can have one or two lone electron pairs. It was stated that a sulfur with one lone electron pair is formally equivalent to a BH^{2-} group and contributes three orbitals and four electrons to the skeleton but a sulfur with two lone electron pairs is equivalent to a BH_2^- group and contributes only two electrons and two orbitals to the skeleton. This latter contention raised confusion regarding the correct classification (nido or arachno) of certain "dual behavior" heteroboranes. It was argued that the nido classification corresponded to a 2370 topology and the arachno to a 2532 topology. It is the purpose of this correspondence to suggest that both BH^{2-} and BH_2^- groups formally contribute three orbitals and four electrons to framework bonding so that regardless of the topological formulation, the arachno classification is correct for 6,8-$S_2B_7H_9$ and related "dual behavior" heteroboranes.

The PERC [paradigm for the electron requirements of clusters[3]] formalism used for the closo, nido, and arachno classifications relies on electron-counting rules developed by Williams, Wade, and Rudolph.[3-5] As has been pointed out previously, bridge hydrogens and BH_2 groups formally amount to protonated framework electrons.[3] For instance, the *nido*-7,8-$C_2B_9H_{11}^{2-}$ can be singly or doubly protonated to give 7,8-$C_2B_9H_{12}^-$ or 7,8-$C_2B_9H_{13}$, respectively, without changing

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