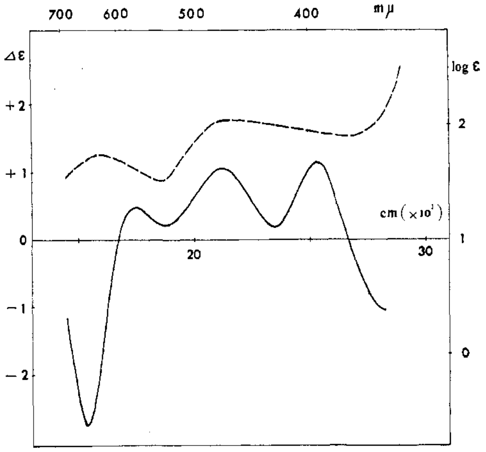


Figure 1.—Absorption spectrum (— — —) and circular dichroism (———) of [$CoCl_2$(*d,d*-3,8-Dimetrien)]Cl.

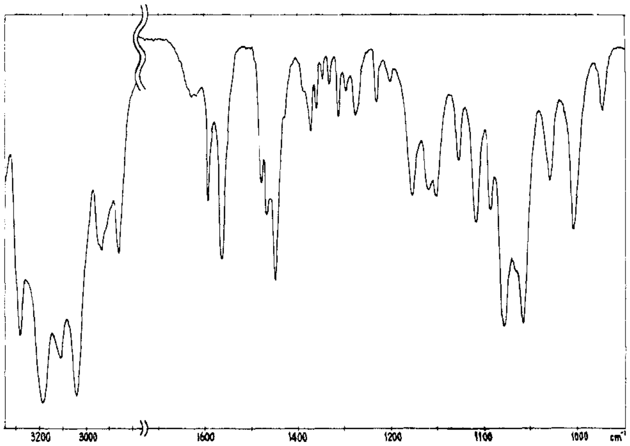


Figure 2.—Infrared spectrum of [$CoCl_2$(*dl*-5-Metrien)]Cl.

tinct circular dichroism bands with opposite sign in the 15,000–18,000 cm^{-1} region which is usually assigned to the electronic transition of $^1A_{1g} \rightarrow {}^1E_a$. For *trans*-[Co(*l*-pn)$_2$$Cl_2$]Cl, only a single transition (16,400 cm^{-1}) was observed.[9] Assuming C_2 or D_2 symmetry, the ^1E_a energy level for D_{4h} symmetry degrades to ^1A and ^1B intrinsically. In *trans*-[Co(*l*-pn)$_2$$Cl_2$]$^+$,[9] the energy levels are so close that only one circular dichroism band appears at 16,400 cm^{-1}. But in *trans*-[Co(*d,d*-3,8-Dimetrien)Cl_2]$^+$, the great distortion causes the energy levels to be further apart as two circular dichroism bands of opposite sign are observed.

As is shown in Figure 2, the infrared spectrum of the purple salt, [$CoCl_2$(*dl*-5-Metrien)]Cl, has four strong absorptions in the 3300–3000 cm^{-1} (N–H stretching) region, two medium absorptions near 1600 cm^{-1} (N–H antisymmetric deformation), and two strong and two medium absorptions at 1090–990 cm^{-1}. Buckingham and Jones[8] identified the three geometrical isomers of the dichlorotrien–cobalt(III) complex according to their infrared spectra. On the basis of these assignments, it may be possible to assign the purple salt as the so-called *cis*-β isomer. This assignment is supported by the absorption spectrum.

CONTRIBUTION FROM THE CHEMISTRY RESEARCH LABORATORY,
AEROSPACE RESEARCH LABORATORIES, WRIGHT-
PATTERSON AIR FORCE BASE, OHIO, AND THE DEPARTMENT
OF CHEMISTRY, UNIVERSITY OF CALIFORNIA, SAN DIEGO,
LA JOLLA, CALIFORNIA

The Metal Ion Reduction of Tris(2,4-pentanedionato)cobalt(III)

BY R. G. LINCK[1] AND J. C. SULLIVAN[2]

Received August 8, 1966

Of the many reactions involving reduction of Co(III) complexes by Cr^{2+}(aq) that have been studied kinetically, only a few have been shown by product analysis to proceed by the outer-sphere mechanism. In each of the two outer-sphere cases where V^{2+}(aq) and Eu^{2+}(aq) have also served as reducing agents, it has been observed that the relative rates of reduction by Cr^{2+}(aq), V^{2+}(aq), and Eu^{2+}(aq) are nearly constant. During an investigation of the Cr(II) reduction of tris(2,4-pentanedionato)cobalt(III), Co(aa)$_3$, in aqueous ethanol,[3] it was observed that Co(aa)$_3$ has a sufficient solubility in aqueous acid to make feasible the determination of the reaction kinetics of Cr^{2+}(aq), V^{2+}(aq), and Eu^{2+}(aq) toward this neutral Co(III) oxidant. The results in this case, where the Co(III) complex has oxygen as donor atoms, can then be compared with the previously studied outer-sphere systems, where nitrogen atoms are the donor atoms.

The results of this study indicate that the reduction of Co(aa)$_3$ by Cr^{2+}(aq) proceeds at least partially by an inner-sphere mechanism; however, the agreement between the rates of reduction by V^{2+}(aq) and Eu^{2+}(aq), relative to Cr^{2+}(aq), for Co(aa)$_3$ and tris(ethylenediamine)cobaltic ion, Co(en)$_3$$^{3+}$, respectively, as oxidants suggests that the outer-sphere path may also be present.

Experimental Section

Tris(2,4-pentanedionato)cobalt(III) was prepared from $CoCO_3$ and acetylacetone, Haa, with PbO_2 as the oxidant. This mixture was shaken overnight and extracted with benzene, and the organic layer was evaporated to give crude Co(aa)$_3$. The compound was purified as described in the literature.[4] Several preparations gave identical kinetic results. *Anal.* Calcd: C, 50.58; H, 5.90; Co, 16.55. Found for two preparations, respectively: C, 50.72, 50.79; H, 5.83, 5.85; Co, 16.30, 16.62. That a true solution of the oxidant in aqueous acid existed was verified by obtaining data that fit Beer's law, over the concentration range used in this study, at 5967 A (ε 129) and 3240 A (ε 7760). Europous ion was prepared from perchloric acid and $EuCO_3$[5] and was stored in a CO_2 atmosphere. Vanadium pentoxide[6] and $Cr(ClO_4)_3 \cdot 6H_2O$[7] were reduced by amalgamated zinc in perchloric acid, and the solutions of the divalent ions were stored in a nitrogen atmosphere. Stock solutions of the reductants were standardized spectrophotometrically by reactions with excess

---

(1) Chemistry Department, University of California, San Diego, La Jolla, Calif.

(2) Chemistry Division, Argonne National Laboratory, Argonne, Ill.

(3) R. G. Linck and R. E. Sievers, to be submitted.

(4) B. E. Bryant and W. C. Fernelius, *Inorg. Syn.*, **5**, 188 (1957).

(5) R. A. Cooley and D. M. Yost, *ibid.*, **2**, 69 (1946).

(6) E. H. Appleman and J. C. Sullivan, *J. Phys. Chem.*, **66**, 442 (1962).

(7) C. Postmus and E. L. King, *ibid.*, **59**, 1208 (1955).

Cr(VI) for Cr(II) and Eu(II) and excess $[Co(NH_3)_5OCOCH_3]^{2+}$ for V(II).

The kinetic runs were carried out by deoxygenating and thermostating all the components (H^+, Na^+, $Co(aa)_3$ in perchloric ion medium) except the reducing agent in a two-necked, serum-capped 50-mm cylindrical spectrophotometer cell. The reductant was added with a syringe, and the extent of reaction was determined with a Cary Model 14 recording spectrophotometer. The wavelength of observation varied over the range 3200–3650 A. The values of the rate constants for individual runs were obtained using a nonlinear least-squares computer program.[8]

The identification of $Cr(aa)^{2+}(aq)$ was accomplished by warming various mole ratios of Cr(III) (as its NO_3^- salt) and Haa in ethanol and allowing these to stand overnight. The solutions were then analyzed spectrophotometrically; a curve of absorbance *vs.* mole ratio showed breaks at Haa/Cr(III) of 1 and 2. The compounds formed at Haa/Cr(III) = 1.5 were separated by ion-exchange chromatography; the two compounds behaved as typical +2 and +1 ions, respectively, and their spectra agreed with that found at Haa/Cr(III) = 1.0 and 2.0, respectively. Extinction coefficients were determined by spectral analysis, followed by decomposition to Cr(VI) and determination of chromium spectrophotometrically. No $Cr(aa)_3$, which was independently synthesized, was found in these experiments.

Results and Discussion

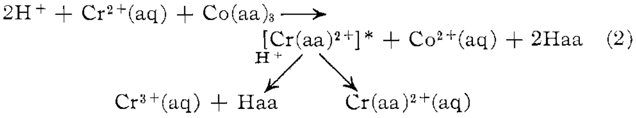
Table I contains a summary of the average values of the rate constants. The precision[9] varied markedly with the three reductants: with $Cr^{2+}(aq)$ the largest spread between duplicate samples was 2%; with $Eu^{2+}(aq)$ the standard deviation for a set of 10 experiments was 8%; with $V^{2+}(aq)$ the standard deviation for a set of 12 experiments was 16%. Two different sources of V(II) were prepared without eliminating this scatter.

Three comments about the data in Table I can be made: (1) There are no significant paths involving H^+ with any of the reductants. (2) Chloride ion at the concentration levels produced by $Eu^{2+}(aq)$ reduction of perchlorate ion[10] does not significantly affect the rate constants. (3) Increase in total ionic concentration increases the rate of reaction when $Cr^{2+}(aq)$ is the reductant.

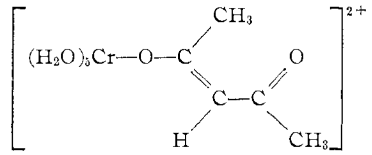
To determine the stoichemistry of the reaction of $Cr^{2+}(aq)$ with $Co(aa)_3$, 78 μmoles of $Co(aa)_3$ and 177 μmoles of $Cr^{2+}(aq)$ were mixed in 200 ml of 0.1 *N* $HClO_4$ and allowed to stand until reaction was complete. The excess $Cr^{2+}(aq)$ was then oxidized with air, and the products were separated on an ion-exchange column (Dowex 50-W-X8 in H^+ form). Of the 233 μmoles of aa^- present initially, 204 were found (spectrophotometrically) as free Haa and 26 as $Cr(aa)^{2+}$(aq); similarly, corresponding to the 78 μmoles of Co(III) present initially, 26 μmoles of $Cr(aa)^{2+}(aq)$ and 60 μmoles of $Cr(H_2O)_6^{3+}$ were recovered; the remainder of the Cr(III) was left on the column in the form of dimeric Cr(III) species. These data indicate that the stoichiometry of the reaction is

$$Cr^{2+}(aq) + Co(aa)_3 + 2.66H^+ \longrightarrow 0.34Cr(aa)^{2+}(aq) + 0.66Cr(H_2O)_6^{3+} + 2.66Haa + Co^{2+}(aq) \quad (1)$$

and that the reduction proceeds 34% by the inner-sphere mechanism and 66% by the outer-sphere. This conclusion is not, however, definite. While there is evidence that free Haa does not coordinate to Cr(II) before the electron transfers (added Haa does not change the amount of chromium acetylacetonate product) and that $Cr^{2+}(aq)$ does not rapidly cause aquation of $Cr(aa)^{2+}(aq)$, there is no assurance that the reduction does not proceed by an inner-sphere mechanism such as shown in reaction 2, where $[Cr(aa)^{2+}]^*$ is some unstable form—for instance, an unchelated complex



$$2H^+ + Cr^{2+}(aq) + Co(aa)_3 \longrightarrow [Cr(aa)^{2+}]^* + Co^{2+}(aq) + 2Haa \quad (2)$$
$$[Cr(aa)^{2+}]^* \xrightarrow{H^+} Cr^{3+}(aq) + Haa \qquad [Cr(aa)^{2+}]^* \longrightarrow Cr(aa)^{2+}(aq)$$



A

It might be argued that at high acid concentration the path for collapse of A to $Cr(aa)^{2+}(aq)$ would be diminished.[11] Accordingly, experiments similar to that described above were carried out in 2 *M* $HClO_4$. Yields of $Cr(aa)^{2+}(aq)$ indicated, in three experiments, 14 ± 2% inner-sphere path at this acidity; in a solution with $HClO_4$ at 0.5 *M* and $NaClO_4$ at 1.6 *M*, the yield of $Cr(aa)^{2+}(aq)$ indicated 23% inner-sphere mechanism. While these data are consistent with a

TABLE I

RATE CONSTANTS FOR THE REDUCTION OF $Co(aa)_3$ BY Eu(II), V(II), AND Cr(II) AT 25°

(A) $[Eu(II)]_0 = 3.54–7.56 \times 10^{-5} M$; $[Co(aa)_3]_0 = 2.02–3.92 \times 10^{-5}\ M$

$[H^+]$, *M*	*k*, M^{-1} sec^{-1}		$[H^+]$, *M*	*k*, M^{-1} sec^{-1}	
0.01	2.0×10^3	(7)[a]	0.88	2.2×10^3	(1)
0.02	2.8×10^3	(1)	0.04	2.3×10^3 [b]	(1)
0.12	1.9×10^3	(1)	0.33	3.1×10^3 [c]	(1)

(B) $[V(II)]_0 = 10.3–61.2 \times 10^{-5}\ M$; $[Co(aa)_3]_0 = 0.83–19.6 \times 10^{-5}\ M$

$[H^+]$, *M*	*k*, M^{-1} sec^{-1}		$[H^+]$, *M*	*k*, M^{-1} sec^{-1}	
0.01	160	(1)[a]	0.63	160	(8)
0.23	200	(2)	0.85	220	(3)
0.48	180	(2)	1.10	250	(3)

(C) $[Cr(II)]_0 = 1.16–4.60 \times 10^{-3}\ M$; $[Co(aa)_3]_0 = 1.87–19.5 \times 10^{-5}\ M$

$[H^+]$, *M*	*k*, M^{-1} sec^{-1}		$[H^+]$, *M*	*k*, M^{-1} sec^{-1}	
0.01	2.9	(1)[a]	0.10	6.2[d]	(2)
0.02	3.1	(2)	1.08	5.4	(1)
0.09	3.3	(2)	1.17	5.1	(2)

[a] Number of experiments. [b] $[Cl^-] = 0.032\ M$. [c] $[Cl^-] = 0.321\ M$. [d] $[Na^+] = 0.94\ M$.

---

(8) This program, essentially identical with that of R. H. Moore and R. K. Zeigler, LA-2367, Los Alamos Scientific Laboratory, was compiled by Mr. Julius Becsey of ARL. The authors are grateful for his help.

(9) Individual runs were generally followed to greater than 95% reaction; the fit of the data to the proposed rate law within any given run is good—the per cent standard deviation was seldom greater than 1%, even for the V(II) experiments.

(10) H. Taube, The Robert A. Welch Foundation Conferences on Chemical Research, VI, Houston, Texas, Nov 1962.

(11) A referee suggested this argument.

small H^+-catalyzed decomposition path (of A to Cr^{3+}(aq) and Haa), they are equally consistent with the simultaneous occurrence of inner-sphere and outer-sphere paths.[12] This postulate of the presence of both mechanisms is further supported by a comparison of the relative rate data in Table II; these data suggest that the outer- and inner-sphere paths are in competition: the two oxidants that presumably go by an outer-sphere mechanism, $Co(NH_3)_6^{3+}$ and $Co(en)_3^{3+}$, have relative rates similar to $Co(aa)_3$, and very different from a typical inner-sphere reactant, $Co(NH_3)_5Cl^{2+}$.[13]

TABLE II

RATES OF REDUCTION OF Co(III) COMPLEXES BY Eu(II) AND V(II) RELATIVE TO THE RATE OF REDUCTION BY Cr(II)

Complex	Cr(II)	V(II)	Eu(II)	Ref
$Co(aa)_3$	1	50	440	This work
$Co(NH_3)_6^{3+}$	1	42	220	*a, b*
$Co(en)_3^{3+}$	1	10	250	*b*
$Co(NH_3)_5Cl^{2+}$	1	2.5×10^{-7}	2×10^{-4}	*b, c*

[a] A. Zwickel and H. Taube, *J. Am. Chem. Soc.*, **83,** 793 (1961). [b] J. P. Candlin, J. Halpern, and D. L. Trimm, *ibid.*, **86,** 1019 (1964). [c] J. P. Candlin and J. Halpern, *Inorg. Chem.*, **4,** 766 (1965).

Finally, it is necessary to account for the difference in the results when Cr^{2+}(aq) is oxidized by $Co(aa)_3$ and $Co(en)_3^{3+}$. Considering just the outer-sphere term for the former oxidant, the rate constants differ by a factor of about 10^5. Within the framework of the Marcus theory of outer-sphere electron-transfer reactions,[14] there are four factors that could account for the greater reactivity of $Co(aa)_3$: (1) a smaller electrostatic repulsion; (2) a larger $\Delta F°$; (3) a smaller solvent reorganization term; and (4) a smaller inner-sphere reorganization term. The first factor should increase the rate constant by about 200 upon the change from $Co(en)_3^{3+}$ to $Co(aa)_3$, while little can be said of factors (2) and (3). But the fourth factor, which is operable in both inner-sphere and outer-sphere reactions, may account for the majority of the remaining difference. In reactions in which the electron is transferred to an e_g orbital (in octahedral notation for simplicity), the stretching of bonds—the inner-sphere reorganization free energy—is anticipated to be very important; thus the weaker bonding (lower ligand field) of O donor ligands relative to N donor ligands leads to an increased rate in the former case. This is illustrated in the reactions of Fe^{2+}(aq) with $Co(H_2O)_5Cl^{2+}$ ($k > 5000$ M^{-1} sec^{-1})[15] and $Co(NH_3)_5Cl^{2+}$ ($k = 16 \times 10^{-4}$ M^{-1} sec^{-1});[16] and Cr^{2+}(aq) with $Cr(H_2O)_5Cl^{2+}$ ($k = 9$ M^{-1} sec^{-1} at 0°)[17] and $Cr(NH_3)_5Cl^{2+}$ ($k = 0.051$ M^{-1} sec^{-1})[18,19] and in the data presented here.

Acknowledgment.—The authors wish to thank Dr. Leonard Spialter of Aerospace Research Laboratories for the use of the Cary Model 14 spectrophotometer.

---

[12] If the entire ionic strength effect is postulated to arise from the outer-sphere path, then at $H^+ = 2$ M one expects 15% inner-sphere path (see Table I). There is no reason to believe that Na^+ and H^+ will have equal effects at 2 M ionic strength. Finally, there is good evidence that the Cr^{2+} ion is bound to more than one oxygen of the Co(III) complex, at least in ethanol–water mixtures—$Cr(aa)_2^+$ is a product of the reaction.[3] However, there is no compelling evidence that the position of the attack of Cr^{2+}(aq) is only at an oxygen and not also at the ring $\geqslant$CH group, a known nucleophilic site. See C. Djordjevic, J. Lewis, and R. S. Nyholm, *Chem. Ind.* (London), 122 (1959); J. P. Collman, *Angew. Chem. Intern. Ed. Engl.*, **4,** 132 (1965).

[13] It is to be noted, in addition, that the value of the rate constant for the V^{2+}(aq) reduction of $Co(aa)_3$ is probably too fast for inner-sphere attack—there is not sufficient time to remove a water molecule from the first coordination sphere of V^{2+}(aq): W. Kruse, quoted in M. Eigen and R. G. Wilkens, "Mechanisms of Inorganic Reactions," Advances in Chemistry Series, No. 49, American Chemical Society, 1965; H. Taube, private communication.

[14] A review is available: R. A. Marcus, *Ann. Rev. Phys. Chem.*, **15,** 155 (1964).

[15] T. J. Conocchioli, G. H. Nancollas, and N. Sutin, *J. Am. Chem. Soc.*, **86,** 1453 (1964).

[16] H. Diebler and H. Taube, *Inorg. Chem.*, **4,** 1029 (1965).

[17] D. L. Ball and E. L. King, *J. Am. Chem. Soc.*, **80,** 1091 (1958).

[18] A. E. Ogard and H. Taube, *ibid.*, **80,** 1084 (1958).

[19] This comparison illustrates the argument with considerable rigor: the electrostatic term is identical; the $\Delta F°$ term favors the amine complex; the solvent reorganization term is expected to be as close to the same as one can achieve—same radii, NH_3 and H_2O presenting roughly the same features toward the solvent, except for the unshared electron pair on the oxygen.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
IOWA STATE UNIVERSITY, AMES, IOWA

Polycyclic Group V Ligands. III. 2,6,7-Trimethyl-4-methyl-2,6,7-triaza-1-phosphabicyclo[2.2.2]octane. A Bidentate Donor[1]

BY B. L. LAUBE, R. D. BERTRAND, G. A. CASEDY,
R. D. COMPTON, AND J. G. VERKADE[2]

Received August 10, 1966

Two types of polycyclic aminophosphine and aminoarsine systems have appeared in the literature since 1960.[3,4] The first described is of the adamantane type, $M_4(NCH_3)_6$, and the second is of the bicyclo[2.2.2]octane structure type, $M(N(CH_3)N(CH_3))_3M$, where M = P or As. We report here the first example of a monophosphorus bicyclic aminophosphine, 2,6,7-trimethyl-4-methyl-2,6,7-triaza-1-phosphabicyclo[2.2.2]octane (I), a number of its derivatives, its arsenic analog, and some unusual bidentate donor properties of I not observed for the comparable open-chain system $P(N(CH_3)_2)_3$.

Experimental Section

Elemental analyses were carried out by Galbraith Laboratories, Inc., Knoxville, Tenn. Molecular weights were obtained on an Atlas CH4 single-focusing mass spectrometer using a source temperature at 200°, a high-temperature inlet system between 145 and 150°, and an energy of 70 ev. The analytical data are recorded in Table I. Proton nmr data shown in Table II were obtained on approximately 5–10% solutions in specified solvents employing either a Varian A-60 or HR-60 spectrometer using tetramethylsilane as an internal standard.

---

[1] For part II in this series see K. J. Coskran and J. G. Verkade, *Inorg. Chem.*, **4,** 1655 (1965).

[2] Alfred P. Sloan Fellow.

[3] J. Riess and J. R. Van Wazer, *Bull. Soc. Chim. France*, 1846 (1966).

[4] D. S. Payne, H. Noth, and G. Henniger, *Chem. Commun.*, 327 (1965), and references therein.