

Reaction of Complex 1 with Lithium Aluminum Hydride. Complex **1** (2.55 g, 3.8 mmol) was added to a stirred suspension of 1.10 g (30 mmol) of lithium aluminum hydride in 30 ml of dry ether at -40° . Black palladium metal separated immediately. After 10 min the solution was allowed to warm to 20° and filtered; when the solvent was removed a pale yellow oil remained. This was analyzed by vpc and found to contain, in addition to a little HMB, one major component (*ca.* 90%) and two minor ones (*ca.* 5%). The mixture was separated by preparative vpc on a column of 20% SE-30 at 120° . The major product eluted first (retention time 19 min) and was identified as ethylpentamethylcyclopentadiene (**12**) by analysis and nmr. *Anal.* Calcd for $C_{12}H_{20}$: C, 87.73; H, 12.27; mol wt, 164. Found: C, 87.81; H, 12.15; mol wt, 164 (mass spectroscopic). Nmr in $CHCl_3$: δ 0.26 (t, $J_{HH} = 6.5$ Hz, 3 H), 0.87 (s, 3 H), 1.40 (q, $J_{HH} = 6.5$ Hz, 2 H), 1.66 (d, $J_{HH} = 6.5$ Hz, 6 H), 1.77 (d, $J_{HH} = 6.5$ Hz, 6 H).

The second fraction was a colorless oil of insufficient quantity for analysis. The third fraction was also obtained in minute yield, but its nmr spectrum was similar to that reported⁴ for *endo*-H-4-methylene-1,2,3,5,6-pentamethylbicyclo[3.1.0]hex-5-ene (**13**). Nmr in $CHCl_3$: δ 0.67 (q, $J_{H-Me} = 6$ Hz, 1 H, *endo*-H at C_2), 0.95 (d, $J_{Me-H} = 6$ Hz, 3 H, *exo*-methyl at C_2), 1.05 (s, 3 H), 1.14 (s, 3 H), 1.59 (q, $J_{HH} = 6.5$ Hz, 2 H), 1.75 (q, $J_{HH} = 6.5$ Hz, 2 H), 4.64 (d, 1 H), 4.67 (d, 1 H).

Reaction of Complex 1 with Hydrazine. A solution of complex **1** (0.68 g, 1 mmol) in 25 ml of benzene at 5° was treated with 0.64 ml (20 mmol) of anhydrous hydrazine. Metal was precipitated immediately; this was filtered off and the solvent removed. The resultant oil (crude) was found to contain only VCP by nmr.

Reaction of Complex 1 with Bromine. A solution of 0.1 mmol of bromine in chloroform at -78° was added to a solution of 0.05 mmol of complex **1** in chloroform at -78° . The resultant solution was studied by nmr over the temperature range -50 to $+20^\circ$. At -50° six broad peaks at δ 1.29, 1.55, 1.71, 1.81, 1.97, and 2.03 were observed. These underwent little change up to *ca.* -15° when a sharp singlet, at δ 2.23, due to HMB began to appear. This grew rapidly with increase in temperature, until by $+20^\circ$ this was the only remaining resonance. A small amount of brown

solid precipitated slowly during the course of reaction. Iodine reacted entirely analogously.

Reaction of Complex 1 with Ethanol. A solution of **1** was allowed to decompose in ethanol over 24 hr. Metal was formed and was filtered off. The solvent was removed to leave an oil. Nmr analysis showed the presence of HMB (*ca.* 8%) and 1-acetylpentamethylcyclopentadiene (**14**) only. The latter was identified by a positive iodoform reaction, its nmr spectrum,²⁹ and that of its 2,4-dinitrophenylhydrazone. Nmr of **14** in $CDCl_3$ (60 MHz): δ 1.09 (s, 3 H), 1.59 (s, 3 H), 1.61 (d, $J_{HH} = 6.5$ Hz, 6 H), 1.87 (d, $J_{HH} = 6.5$ Hz, 6 H). *Anal.* Calcd for $C_{12}H_{18}O$: C, 80.85; H, 10.18. Found: C, 80.58; H, 10.13.

The dinitrophenylhydrazone showed resonances ($CDCl_3$, 60 MHz) at δ 1.26 (s, 3 H), 1.45 (s, 3 H), 1.69 (d, 6 H), 1.88 (d, 6 H), as well as aromatic protons at δ 8.14 (s, 1 H), 8.26 (d, $J_{HH} = 2.5$ Hz, 1 H), 9.13 (d, $J_{HH} = 2.5$ Hz, 1 H).

An entirely analogous reaction occurred when complex **1** was stirred with methanol.

Reaction of Complex 1 with *o*-Phenanthroline. *o*-Phenanthroline (0.36 g, 2 mmol) was added to a solution of 0.34 g (0.5 mmol) of complex **1** in 10 ml of benzene. A bright yellow precipitate formed immediately. Stirring was continued for 30 min; the precipitate was filtered off and washed with benzene. After drying, 0.58 g of a yellow powder, containing the complex **11** and *o*-phenanthroline hydrochloride, was obtained. This was carefully recrystallized several times from benzene to give the pure complex, 1-(chloro-*o*-phenanthroline)palladiumvinylpentamethylcyclopentadiene as small crystals, mp $200-210^\circ$ dec. *Anal.* Calcd for $C_{24}H_{22}ClN_2Pd$: C, 59.64; H, 5.21; Cl, 7.34; N, 5.80; Pd, 22.02. Found: C, 58.63; H, 5.19; Cl, 7.48; N, 5.91; Pd, 21.85. Nmr in $CDCl_3$: δ 1.38 (s, 3 H), 1.64 (s, bd, 6 H), 1.82 (s, bd, 6 H), 4.70 (d, $J_{HH} = 1.5$ Hz, 1 H), 4.89 (d, $J_{HH} = 1.5$ Hz, 1 H).

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Carbon Dioxide Catalysis of Reactions of Chromium(III). I. Oxygen Exchange of Hydroxopentaamminechromium(III) Ion

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Abstract: Carbon dioxide catalyzes the exchange of oxygen between $Cr(NH_3)_5OH^{2+}$ and solvent water. At 25° in buffered perchlorate solutions of ionic strength 0.1, the rate of exchange is rate = $k_1[Cr(NH_3)_5OH_2^{3+}] + (k_2 + k''')[CO_2][Cr(NH_3)_5OH^{2+}]$, where k_1 is $6.3 \times 10^{-3} \text{ sec}^{-1}$, k_2 is $17 \times 10^{-3} \text{ sec}^{-1}$, and k''' is $7 \text{ M}^{-1} \text{ sec}^{-1}$. Also, ^{18}O introduced as HCO_3^{*-} rapidly appears in $Cr(NH_3)_5OH^{2+}$. These results require a mechanism involving formation of a carbonato- $Cr(III)$ complex and quite rapid scrambling of the oxygen atoms of this complex.

Carbonato species of $Co(III)$ are well known¹ and stable but no authenticated carbonato complex of $Cr(III)$ has been described.² Attempts to prepare such complexes generally produce Cr_2O_3 . CO_2 is an efficient catalyst for decomposition of chromium-ammine complexes, but also catalyzes other substitution reactions on $Cr(III)$.

In a study of $Cr(III)$ substitution reactions³ an unusual pH dependence of the rate of oxygen exchange of

$Cr(NH_3)_5OH^{2+}$ was noted. This was traced to CO_2 catalysis and we now report a study of this catalytic reaction. This provides a mechanism which unifies otherwise puzzling aspects of $Cr(III)$ chemistry.

Experimental Section

Water triply distilled from quartz was employed. $NaClO_4$ solutions, prepared by neutralization of $HClO_4$, were digested at 80° and pH 8 for several hours, thereby coagulating a fine precipitate (probably SiO_2), which was removed by filtration. CO_2 was purified prior to mass spectrometric analysis by gas chromatography. Solutions were protected from atmospheric CO_2 by "Lithasorb" contained in drying tubes connected to air vents.

(1) C. R. P. MacColl, *Coord. Chem. Rev.*, **4**, 147 (1969).

(2) "Gmelins Handbuch der Anorganische Chemie," Springer Verlag, Berlin, System No. 52: Part A, 1963; Part B, 1962; Part C, 1965.

(3) N. V. Duffy and J. E. Earley, *J. Amer. Chem. Soc.*, **89**, 272 (1967).

Consolidated-Nier 21-200 and AEI MS-10 mass spectrometers were used. Repetitive measurements of the 46/44 isotopic abundance ratio agreed to better than 0.5% or 1%, respectively.

Aqueous NaClO₄ media of normal isotopic composition, sometimes containing added acetate buffers or NaHCO₃, were kept in amber vessels in a water bath to establish thermal equilibrium. The reaction was initiated by adding solid oxygen-18 labeled aquopentaamminechromium(III) perchlorate. Aliquots (65–75 ml) of the solution were removed at various times and quenched by adding the aliquot to 5–6 ml of 9.5 M perchloric acid which had been precooled in a Dry Ice–acetone bath. A precooled solution of 25–30 ml of 11 M perchloric acid saturated with sodium perchlorate was added in two portions accompanied by rapid swirling in a Dry Ice–acetone bath. Precipitated aquopentaamminechromium(III) perchlorate was either separated immediately on a medium-porosity sintered glass filter or, during fast reactions, stored in a water–alcohol slush bath at –20° prior to filtration. Filtered solid was washed with 5 ml of 95% ethanol and two 3-ml portions of anhydrous ether and transferred to a Urey tube containing 0.1 g of purified potassium thiocyanate. This mixture was evacuated for at least 12 hr. The Urey tube was closed and heated until the potassium thiocyanate melted (mp 173°). Care was taken not to heat the tube to 300°, the temperature at which aquopentaamminechromium(III) perchlorate explodes. Thiocyanate ion displaces water in aquopentaamminechromium(III) ion with the complex changing color from orange to purple. Water was distilled into a 5–6-mm thin-walled glass tube containing 10–20 mg of purified guanidine hydrochloride. From this point the conversion of water to carbon dioxide followed a standard procedure closely.⁴

A Metrohm Model E 336A potentiograph was used to record titration curves. The pH at the point of half neutralization was taken as the apparent pK_a of Cr(NH₃)₅H₂O.³⁺

Results

Table I lists values of the apparent pK_a of Cr(NH₃)₅H₂O³⁺ under the conditions of the water-exchange experiments. If a stable complex between CO₂ and Cr(NH₃)₅OH²⁺ were formed, the apparent pK_a of the aquo ion should be a function of [CO₂]. The data in Table I are not consistent with the formation of a complex with a formation constant greater than 100 M⁻¹. CO₂ catalysis of decomposition of Cr(NH₃)₅OH²⁺ prevented valid measurements at higher CO₂ concentrations.

Table I. Apparent pK_a of Cr(NH₃)₅H₂O³⁺^a

[CO ₂], mM	pK _a
0.00	4.85 ± 0.02 ^b
0.34	4.84
0.63	4.77
0.67	4.82
0.72	4.85

^a Temperature, 25.0°, μ = 0.10 M (NaClO₄). ^b Ten determinations.

Presence of CO₂ caused a slight immediate intensification of visible and ultraviolet absorption for solutions of Cr(NH₃)₅H₂O³⁺ which had been adjusted to pH 4.9. A much slower change, such as would be expected to accompany formation of a tetraammine–Cr(III) species, was also observed. The rapid change is consistent with weak (K_f < 100) complex formation but does not establish the existence of such a complex.

Figure 1 displays McKay plots for loss of ¹⁸O from Cr(NH₃)₅H₂O³⁺ in aqueous solution and Table I lists first order water-exchange rate constants computed from slopes of plots of this sort. Zero-time intercepts corresponded with independent measurements of substrate

(4) P. D. Boyer, D. J. Graves, C. H. Suelter, and M. E. Dempsey, *Anal. Chem.*, **33**, 1906 (1961).

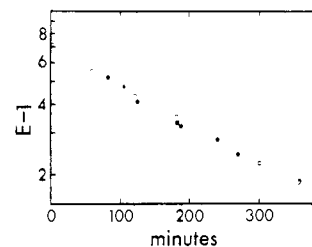


Figure 1. Experimental data for runs 3 (○), 6 (●), and 7 (■). Conditions given in Table I. The enrichment, *E*, is obtained by dividing the 46/44 isotope abundance ratio of CO₂ prepared from the aquo ion by the 46/44 ratio of CO₂ prepared from normal water.

enrichment, so that no separation-induced exchange occurs.

Since ample time was allowed for equilibration of carbonate species before addition of substrate and all experiments were carried out at a pH below 6, CO₂ is the dominant carbonate form present. As Figure 2 shows, CO₂ is an efficient catalyst for ¹⁸O exchange and this catalysis is greater in more basic solution.

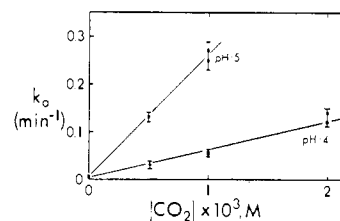


Figure 2. Dependence of observed rate constant on carbon dioxide concentration and pH. Conditions as in Table I.

These data (Table II) are fitted by the rate law

$$\text{rate} = k_1[\text{Cr}(\text{NH}_3)_5\text{OH}_2]^{3+} + (k_2 + k''[\text{CO}_2])[\text{Cr}(\text{NH}_3)_5\text{OH}^{2+}]$$

where 4.85 has been used as the pK_a of Cr(NH₃)₅OH²⁺ (Table I). At 25°, μ = 0.1 M, k₁ is 6.3 ± 0.5 × 10⁻⁵ sec⁻¹, in good agreement with the value previously reported.³ At pH 4, k'' is 7.2 M⁻¹ sec⁻¹ and at pH 5, k'' is 7.3 M⁻¹ sec⁻¹. The value of k₂ consistent with the data is 17 ± 4 × 10⁻⁵ sec⁻¹; since this value assumes that CO₂ was totally absent in runs 9 and 16, it must be considered as only an upper limit on the rate of O exchange of Cr(NH₃)₅OH²⁺. By analogy with the Co(III) case,⁵ a somewhat lower value might be expected. Runs 9 and 10 indicate that the variation of buffer concentration does not cause a serious effect.

Although neither spectrophotometric nor titrimetric studies gave definite evidence of (Cr(NH₃)₅OH·CO₂)²⁺ complexes, the strong catalysis of the water-exchange reaction suggests involvement of such a species. Figure 3 displays the results of an experiment in which non-labeled Cr(NH₃)₅H₂O³⁺ and labeled CO₂ were employed. Substantial incorporation of the CO₂ oxygen into Cr(NH₃)₅OH²⁺ was complete 2 min after mixing, and subsequent loss of label to the solvent occurred at the same rate as observed when the label was introduced as Cr(NH₃)₅O*H²⁺.

If incorporation of CO₂ were complete and instantaneous, the maximum intercept of Figure 3 would be near

(5) H. R. Hunt and H. Taube, *J. Amer. Chem. Soc.*, **80**, 2642 (1958).

Co(III) complexes. Also, water exchange of $\text{Co}(\text{NH}_3)_5\text{OH}^{2+}$ is slower than that of $\text{Co}(\text{NH}_3)_5\text{OH}_2^{3+}$ and no CO_2 catalysis has been noted,⁵ although the carbonate complexes of Co(III) are stable.¹ These results imply that the flip process is less likely for Co(III) than for Cr(III). This may be attributed to the greater tendency of d^8 ions, relative to d^6 ions, to adopt seven-coordinate structures.^{9,10}

This also may account for the marked difference between the oxygen exchange behavior of $\text{Cr}(\text{C}_2\text{O}_4)_3^{3-}$ (all 12 oxygens equivalent) and $\text{Co}(\text{C}_2\text{O}_4)_3^{3-}$ (6 oxygens exchange more rapidly, 6 more slowly).¹¹ Rapid intra-

(9) A structure similar to that required for the intermediate has, however, been suggested for certain Co(III) carboxylato complexes: R. T. M. Frazer, *Nature*, **202**, 691 (1964).

(10) S. T. Speers, J. R. Perumareddi, and A. W. Adamson, *J. Amer. Chem. Soc.*, **90**, 6626 (1968).

molecular oxygen exchange may occur in $\text{Cr}(\text{C}_2\text{O}_4)_3^{3-}$ without one-ended dissociation.¹²

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(11) J. A. Broomhead, I. Lauder, and P. Nimmo, *Chem. Commun.*, 652 (1969).

(12) C. A. Bunton, J. H. Carter, D. R. Llewellyn, C. O'Connor, A. L. Odell, and S. Y. Yih, *J. Chem. Soc.*, 4615 (1964).

Dithiotropolonates. II.¹ The Synthesis and Properties of Dithiotropolone and Its Metal(II) Complexes

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Abstract: Dithiotropolone (**15**) has been prepared in *ca.* 30% yield from tropolone *via* the reaction of hydrosulfide ion with 1,2-diethoxytropylium tetrafluoroborate (**13**) and isolated as deep red, air-sensitive crystals. Infrared, electronic, and mass spectral characterization data are reported. The tropylium species **13** has been shown to be a potentially valuable intermediate in the synthesis of 1,7-disubstituted 1,3,5-cycloheptatrienes. Reactions with primary amines alone and with hydrosulfide yield *N,N*-disubstituted aminotropoloneimines (**16**, **17**) and *N*-substituted aminothiotropolones (**18**), respectively, in 40–75% yield. Dithiotropolone or its sodium salt readily reacts with divalent metal salts to afford a series of intensely colored, slightly soluble bis-chelate complexes, $\text{M}(\text{SST})_2$ (**7**, **8**). Probable ground-state electronic structures of these complexes are discussed in relation to neutral bis(dithiolene) complexes (**1**). Spectral and polarographic studies reveal that, like the dithiolenes, $\text{M}(\text{SST})_2$ species ($\text{M} = \text{Ni}, \text{Pd}, \text{Pt}$) exhibit intense near-infrared absorption bands and are reducible in two apparent one-electron processes, which, in contrast to those of the dithiolenes, are irreversible and occur at potentials *ca.* 0.75–1.0 V more negative. Electrochemical activity has also been established for $\text{Cu}(\text{SST})_2$, $\text{Zn}(\text{SST})_2$, $\text{Cd}(\text{SST})_2$, and for Ni and Zn complexes of 2-mercaptotropolone, *N,N*-dimethylaminotropoloneimine, and *N*-methylaminotropolone; in most cases the redox processes are irreversible. The presently available information does not permit a detailed assessment of the relation between electronic structures of dithiolene and dithiotropolonate complexes, the latter of which are under further investigation.

The chemistry of metal complexes in which all ligating atoms are sulfur has undergone a most significant advance in recent years. Numerous new species containing four-, five-, and six-membered chelate rings have been prepared, but perhaps the most striking developments have occurred as a consequence of the extensive investigations of those complexes possessing unsaturated five-membered rings of general types **1** and **2** ($\text{X} = \text{Y} = \text{S}$). Such complexes are now generically referred to as dithiolenes^{3a} (or dithienes^{3b,c}). Bisdithiolenes have three properties of general importance: (i) they undergo redox reactions producing an electron transfer series of at least three members, $[\text{M}-\text{S}_4]^{2-} \rightleftharpoons$



$[\text{M}-\text{S}_4]^- \rightleftharpoons [\text{M}-\text{S}_4]^0$; (ii) monomeric complexes (with the probable exception of zinc derivatives) are planar irrespective of oxidation level; (iii) metal-ligand bonding is highly covalent and odd electrons in paramagnetic species are extensively delocalized. The last property is responsible for the well recognized ambiguity in assigning formal oxidation states in $[\text{M}-\text{S}_4]^z$ species with $z = -1, 0$. While most exhaustively demonstrated for dithiolenes, these properties extend to certain $[\text{M}-(\text{NH})_4]^{z+}$,⁴ $[\text{M}-(\text{NH})_2\text{S}_2]^{z+}$,⁵ and $[\text{M}-\text{O}_2\text{S}_2]^{z+}$ ⁶ series of

(1) Part I: C. E. Forbes and R. H. Holm, *J. Amer. Chem. Soc.*, **90**, 6884 (1968).

(2) National Institutes of Health Predoctoral Fellow, 1968–present.

(3) For reviews *cf.* (a) J. A. McCleverty, *Progr. Inorg. Chem.*, **10**, 49 (1969); (b) G. N. Schrauzer, *Transition Metal Chem.*, **4**, 299 (1968); (c) G. N. Schrauzer, *Accounts Chem. Res.*, **2**, 79 (1969); (d) L. F. Lindoy, *Coord. Chem. Rev.*, **4**, 41 (1969).

(4) A. L. Balch and R. H. Holm, *J. Amer. Chem. Soc.*, **88**, 5201 (1966).

(5) R. H. Holm, A. L. Balch, A. Davison, A. H. Maki, and T. E. Berry, *ibid.*, **89**, 2866 (1967).

(6) A. L. Balch, *ibid.*, **91**, 1948 (1969).