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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 CHCl₂; δ 0.26 (t, J_{HH} = 6.5 Hz, 3 H), 0.87 (s, 3 H), 1.40 (q, $J_{\rm HH} = 6.5$ Hz, 2 H), 1.66 (d,³² 6 H), 1.77 (d³², 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 CHCl₃: δ 0.67 (q, $J_{\text{H-Me}} = 6$ Hz, 1 H, endo-H at C₂), 0.95 (d, $J_{Me-H} = 6$ Hz, 3 H, exo-methyl at C₂), 1.05 (s, 3 H), 1.14 (s, 3 H), 1.59 (q,³² 3 H), 1.75 (q,³² 3 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°. 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 2,4dinitrophenylhydrazone. Nmr of 14 in CDCl₃ (60 MHz): δ 1.09 (s, 3 H), 1.59 (s, 3 H), 1.61 (d,³² 6 H), 1.87 (d,³² 6 H). Anal. Calcd for C₁₂H₁₈O: C, 80.85; H, 10.18. Found: C, 80.58; H. 10.13.

The dinitrophenylhydrazone showed resonances (CDCl₃, 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, $J_{\rm HH}$ = 2.5 Hz, 1 H), 9.13 (d, $J_{\rm HH} = 2.5$ 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)palladium)vinylpentamethylcyclopentadiene as small crystals, mp 200–210° dec. Anal. Calcd for $C_{24}H_{25}CIN_2Pd$: 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 CDCl₂: δ 1.38 (s, 3 H), 1.64 (s, bd, 6 H), 1.82 (s, bd, 6 H), 4.70 (d, J_{IIH} = 1.5 Hz, 1 H), 4.89 (d, $J_{\text{HH}} = 1.5$ 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(NH₃)₅OH²⁺ and solvent water. At 25° in buffered perchlorate solutions of jonic strength 0.1, the rate of exchange is rate = $k_1[Cr(NH_3)_5OH_2^{3+}] + (k_2 + k_3)_5OH_2^{3+}]$ k'''[CO₂])[Cr(NH₃)₅OH²⁺], where k_1 is 6.3 × 10⁻⁵ sec⁻¹, k_2 is 17 × 10⁻⁵ sec⁻¹, and k''' is 7 M^{-1} sec⁻¹. Also, ¹⁸O introduced as HCO3* - rapidly appears in Cr(NH3)5OH2+. These results require a mechanism involving formation of a carbonato-Cr(III) complex and quite rapid scrambling of the oxygen atoms of this complex.

arbonato species of Co(III) are well known¹ and Carbonato species of county 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 chromiumammine 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

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

Cr(NH₃)₅OH²⁺ was noted. This was traced to CO₂ 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. NaClO₄ solutions, prepared by neutralization of HClO₄, were digested at 80° and pH 8 for several hours, thereby coagulating a fine precipitate (probably SiO₂), which was removed by filtration. CO₂ was purified prior to mass spectrometric analysis by gas chromatography. Solutions were protected from atmospheric CO2 by "Lithasorb" contained in drying tubes connected to air vents.

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

^{(2) &}quot;Gmelins Hanbuch der Anorganische Chemie," Springer Verlag, Berlin, System No. 52: Part A, 1963; Part B, 1962; Part C, 1965.

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_n of Cr(NH₃)₅H₃O.³⁺

Results

Table I lists values of the apparent pK_a of $Cr(NH_3)_5$ -H₂O³⁺ 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 $Cr(NH_3)_5H_2O^{3+a}$

[CO ₂],m <i>M</i>	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°, $\mu = 0.10 M$ (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 $Cr(NH_3)_{\delta}H_2O^{3+}$ 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 $3(\bigcirc)$, $6(\bigcirc)$, and $7(\blacksquare)$. 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, CO_2 is the dominant carbonate form present. As Figure 2 shows, CO_2 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

rate =
$$k_1[Cr(NH_3)_5OH_2]^{3+} + (k_2 + k'''[CO_3])[Cr(NH_3)_5OH^{2+}]$$

where 4.85 has been used as the pK_a of $Cr(NH_3)_5OH_2^{3+}$ (Table I). At 25°, $\mu = 0.1 M$, k_1 is $6.3 \pm 0.5 \times 10^{-5}$ 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 k_2 consistent with the data is $17 \pm 4 \times 10^{-5}$ 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 $Cr(NH_3)_5OH^{2+}$. 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 $(Cr(NH_3)_5OH \cdot CO_2)^{2+}$ 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 *nonlabeled* $Cr(NH_3)_5H_2O^{3+}$ and *labeled* CO_2 were employed. Substantial incorporation of the CO_2 oxygen into $Cr-(NH_3)_5OH^{2+}$ 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 $Cr(NH_3)_5O*H^{2+}$.

If incorporation of CO_2 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).



Figure 3. Loss of ¹⁸O from Cr(NH₃)₅O*H²⁺ (m*M*) at pH 4.0 for solutions 2 m*M* in CO₂ (filled points, run 14, ¹⁸O introduced as Cr(NH₃)₅O*H²⁺, E = 5, CO₂ as HCO₃⁻, E = 1; open points, run 15, ¹⁸O introduced as HCO₃*⁻, E = 25, Cr(NH₃)₅OH²⁺ initially unlabeled, E = 1 at t = 0). Other conditions are given in Table I, and *E* is defined in Figure 1. The dotted line corresponds to the rate of oxygen exchange of CO₂ with water under these conditions.

16 rather than near 3 as observed. However, in view of the rapid rate of exchange of CO_2 with solvent water it is really quite remarkable that incorporation of ¹⁸O into $Cr(NH_3)_5OH^{2+}$ is observed at all.⁶ No explanation that

 Table II.
 Rate of Oxygen Exchange of Aquopentaamminechromium(III) Ion^a

Run	pH	μ, Μ	$[\text{CO}_2]_{\rm t} \\ \times 10^3, M$	$\frac{k_0 \times 10^5}{\sec^{-1}g}$
1	1.04	0.098	0	6.5 ± 0.5
2 ^b	1.13	0.118	0	6.6 ± 0.5
3	1.13	0.291	0	5.7 ± 0.3
4	1.16	0.077	с	6.0 ± 0.2
5	1.34	0.053	0	6.5 ± 1.0
6	1.49	0.040	0	6.2 ± 0.5
7	1.49	0.041	0.4	6.8 ± 0.5
8	1.92	0.032	0	5.5 ± 0.8
9	4.11^{d}	0.019	0	7.7 ± 0.5
10	4.12°	0.013	0	10 ± 2
11	3.92 ^d	0.100	0.51	46 ± 13
12	3.99 ^d	0.100	1.00	87 ± 7
13	4.10 ^d	0.019	1.00	93 ± 12
14	4.00^{d}	0.100	2.00	233 ± 16
15	4.00ď	0.100	2.02	$200 \pm 17'$
16	4.94^{d}	0.040	0	12 ± 3
17	4.96 ^d	0.100	0.50	217 ± 18
18	5.02^{d}	0.101	1.01	450 ± 30
19	5.02^{d}	0.114	1.00	420 ± 30

^a [Cr(NH₃)₃H₂O³⁺], 1.20 ± 0.01 × 10⁻³ *M*; temperature, 25.0°; [CO₂]_t computed from amount of NaHCO₃ added; aqueous NaClO₄ medium. ^b [Cr(NH₃)₅OH₂³⁺], 7.28 × 10⁻³ *M*. °1.0 m*M* in NaNO₃. ^d Buffered, [CH₃COO⁻] 0.012 *M*, [CH₃COOH] 0.006 *M*. ^e Buffer concentrations half that for run 9. ^f Run with nonlabeled aquopentaamminechromium(III) ion and 24.9 times enriched sodium bicarbonate, [Cr(NH₃)₅H₂O³⁺], 1.37 × 10⁻³ *M*. ^e Errors are estimated from the scatter of points on each run.

we have been able to devise will account for Figure 3 unless it assumes that a carbonato-Cr(III) complex is involved and that internal oxygen exchange in this complex is extremely rapid.

Discussion

Any mechanism for the CO₂ catalysis which would involve competition between CO₂ and H₂O for an intermediate such as $Cr(NH_3)_5^{3+}$ would predict that the rate of formation of this intermediate would be a limiting factor, and therefore such a mechanism could not explain a rate of oxygen exchange much faster than that of $Cr(NH_3)_5OH^{2+}$.

(6) Dr. T. Kallen has repeated these experiments independently and has confirmed the results of Figure 3.

A mechanism which does explain the data is

$$RO^{*}H^{2+} + OCO \stackrel{k_{a}}{\underset{k_{b}}{\longleftarrow}} (RO^{*}O \cdot H)^{2+}$$

$$k_{a} \uparrow \downarrow k_{c}$$

$$ROH^{2+} + OCO^{*} \stackrel{k_{e}}{\underset{k_{f}}{\longleftarrow}} (ROCO^{*} \cdot H)^{2+}$$

By the use of the steady state approximation for the two reactive intermediates $(RO^*CO_2 \cdot H)^{2+}$ and $(ROCO^*O \cdot H)^{2+}$, it can be shown that the rate of loss of oxygen from RO^*H^{2+} in the presence of CO_2 (when $k_f[O^*CO] \approx 0$) is given by

rate =
$$-\frac{d}{dt}[RO^*H] = k_a \times \left[1 - \frac{(k_d + k_e)k_b}{(k_b + k_c)(k_d + k_e) - k_ck_d}\right][RO^*H^{2+}][CO_2]$$
 (1)

Except for a negligible isotope effect, $k_b = k_e$ and, by symmetry, $k_c - 2k_d$. Equation 1 may be simplified by the use of these relationships, and the rate constant for the CO₂ dependent term in the observed rate law may be written

$$k^{\prime\prime\prime} = \frac{2k_{\rm a}k_{\rm c}}{3k_{\rm c} + 2k_{\rm b}} \tag{2}$$

The value of the observed rate constant k''' would therefore be expected to be a function of the ratio of k_c to k_b , approaching $2/3k_a$ when $k_c \gg k_b$ but dropping off rapidly to 0 if k_c were to decrease relative to k_b .

Data presented above indicate that 100 $M^{-1} > K_f = k_a/k_b$. This inequality may be combined with eq 2 and the observed value of k''' (7.3 M^{-1} sec⁻¹) to yield

$$1 > \frac{0.11 \text{ sec}^{-1}}{k_{\rm b}} + \frac{0.073 \text{ sec}^{-1}}{k_{\rm c}}$$
(3)

Since both k_b and k_c are inherently positive quantities, it follows that $k_b > 0.11 \text{ sec}^{-1}$ and $k_c > 0.073 \text{ sec}^{-1}$. This limit for k_b and the limit on K_f implies the limit $k_a > 11 M^{-1} \text{ sec}^{-1}$.

The rate constant (k_a) for the attack of $Cr(NH_3)_4$ -OH²⁺ on CO₂ is therefore several orders of magnitude greater than the rate constant⁷ (3 × 10⁻⁴ M^{-1} sec⁻¹) for attack of H₂O on CO₂. If the reaction of ROH²⁺ with CO₂ is considered a nucleophilic attack on carbon, it would be necessary to conclude that substitution of Cr(NH₃)₅²⁺ for H increases the nucleophilicity of oxygen. This is in accord with the fact that ROH₂³⁺ is a weaker acid than H₃O⁺.

An extraordinary feature of our results is the demonstration of the rapidity of the "flip" of coordinated CO_3^{2-} ($k_c > 0.07 \text{ sec}^{-1}$). No mechanism for this flip which does not involve a seven-coordinated Cr(III) will accord with the fact that oxygen scrambling takes place more rapidly than oxygen exchange with solvent water or loss of NH₃.

Other results⁸ indicate that CO_2 also catalyzes both anation and aquation of Cr(III) ammine complexes, but does not catalyze these reactions for the corresponding

⁽⁷⁾ G. A. Mills and H. C. Urey, J. Amer. Chem. Soc., 62, 1019 (1940); D. M. Kern, J. Chem. Educ., 37, 14 (1960).

⁽⁸⁾ Part II in this series: J. E. Earley, D. J. Surd, L. R. Crone, and D. J. Quane, in preparation; J. E. Earley and D. J. Surd, Inorganic Section, Southeastern Regional Meeting of the American Chemical Society, Richmond, Va., Nov 1969.

Co(III) complexes. Also, water exchange of Co(NH₃)₅-OH²⁺ is slower than that of Co(NH₃)₅OH₂³⁺ and no CO₂ 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 d³ ions, relative to d⁶ ions, to adopt seven-coordinate structures.^{9, 10}

This also may account for the marked difference between the oxygen exchange behavior of $Cr(C_2O_4)_5^{3-}$ (all 12 oxygens equivalent) and $Co(C_2O_4)_3^{3-}$ (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. Spees, J. R. Perumareddi, and A. W. Adamson, J. Amer. Chem. Soc., 90, 6626 (1968).

molecular oxygen exchange may occur in $Cr(C_2O_4)_5^{3-}$ without one-ended dissociation.¹²

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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 aminotroponeimines (16, 17) and Nsubstituted aminothiotropones (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, M-(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, $M(SST)_2$ species (M = Ni, Pd, Pt) exhibit intense near-infrared absorption bands and are reducible in two apparent oneelectron 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 Cu(SST)₂, Zn(SST)₂, Cd(SST)₂, and for Ni and Zn complexes of 2-mercaptotropone, N,N-dimethylaminotroponeimine, and N-methylaminothiotropone; 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 (X = Y = 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, $[M-S_4]^{2-} \rightleftharpoons$



 $[M-S_4]^- \rightleftharpoons [M-S_4]^\circ$; (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 $[M-S_4]^\circ$ species with z = -1, 0. While most exhaustively demonstrated for dithiolenes, these properties extend to certain $[M-(NH)_4]^\circ$, $[M-(NH)_2S_2]^\circ$, and $[M-O_2S_2]^\circ$ series of

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