to either H–C–N coupling or a small difference between axial and equatorial methyl groups, or both. The BH protons gave no observable signals.

Infrared Spectrum.—The vapor-phase infrared spectrum of the cotrimer was recorded by means of the Beckman IR7 instrument, with the cell in an asbestos-board box heated to known temperatures by a heater-blower, all within the cell chamber. The frequencies of the peaks (cm^{-1}) are listed with relative intensities in parentheses, as follows: 3027 (3.7), 3023 sh (2.8), 2991 (6.0), 2947 (7.6), 2897 (1.6), 2854 (1.0), 2555 (0.7), 2545 (1.0), 2453 (16), 2393 (14), 2337 (4.6), 2322 (4.6), 2278 (1.4), 1471 (3.5), 1452 (3.1), 1435 (4.9), 1406 (0.8), 1326 (0.2), 1224 (11), 1173 (13), 1126 (12), 1108 (11), 1078 (6), 1038 (3.0), 963 (3.6), 944 (4.4), 914 (3.0), 883 (1.2), 862 (1.8), 824 (2.4), 804 (1.8), 732 (0.6), 640 (0.7). Most of these peaks can be assigned in the same manner as for $[(CH_3)_2NBH_2]_3$,[2] with the difference that the multiplicity of modes, such as CH_3 stretching, deformation, rocking, and wagging, or similar effects with BH_2, would be due to the different situations of these groups rather than to steric splitting of axial groups or atoms. Neither these results nor the proton nmr spectrum would suggest any steric effects in the cotrimer.

The Trimethylamine Reaction.—A mixture of 0.1075 mmol each of $(CH_3)_3N$ and the cotrimer, heated for 15 min at 100°, showed no reaction, suggesting that a tertiary amine could be used to remove the CH_3SBH_2 by-product. However, after 29 hr in a sealed tube at 100°, 59% of the $(CH_3)_2NBH_2$ units had been liberated as the monomer and dimer, while 57% of the CH_3SBH_2 units appeared as the $(CH_3)_3N$ complex.[4] A 34% disproportionation of $(CH_3)_2NBH_2$ groups was represented by a 0.036-mmol yield of $[(CH_3)_2N]_2BH$, while somewhat more $(CH_3)_3NBH_3$ could be ascribed to this disproportionation and that of the complex $(CH_3)_3NBH_2SCH_3$.

The Diborane Reaction.—Diborane also was not readily reactive toward the cotrimer. Nearly equimolar portions of diborane and the cotrimer (0.24 mmol each) were placed in a vertical stopcocked reaction tube attached to the vacuum line. The lower half of the tube was repeatedly heated for hours at 80–100°, eventually yielding 0.32 mmol of $(CH_3)_2NB_2H_5$, at the cost of 0.205 mmol of diborane.

Acknowledgment.—It is a pleasure to acknowledge the generous support of this research by the Office of Naval Research.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
MASSACHUSETTS INSTITUTE OF TECHNOLOGY,
CAMBRIDGE, MASSACHUSETTS 02139

Effects of Chelate Ring Substituents on the Polarographic Redox Potentials of Tris(β-diketonato)ruthenium(II,III) Complexes

BY GEORGE S. PATTERSON[1] AND R. H. HOLM*

Received March 21, 1972

The effect of substituent variation on the polarographic half-wave potentials for oxidation and reduction of certain general types of organic molecules has been extensively investigated in recent years.[2] In a number of cases these potentials have been linearly correlated with Hammett or Taft substituent parameters. Related studies of coordination and organometallic complexes are considerably less numerous. However, in some instances correlation between various properties of these complexes, such as ligand substituent parameters or basicities and half-wave or half-cell potentials have been found.[3–6] The present study was initiated as a consequence of the somewhat unexpected finding that $Ru(tfac)_3$[7] was readily reduced chemically to $Ru(tfac)_3^-$ and that the corresponding electrochemical process was characterized by a half-wave potential very near 0 V *vs.* sce.[8] The anion could be isolated in the form of a moderately air-sensitive salt. In contrast, the half-wave potential for reduction of $Ru(acac)_3$ was *ca.* 0.8 V more cathodic and well-characterized salts of $Ru(acac)_3^-$ could not be obtained. These results indicated a decided effect of substituents on redox potentials of ruthenium(II,III) tris(β-diketonates), a matter which is explored more fully in this report. Coincident with our recent[8] and present work has been the demonstration that $M(SacSac)_3$ complexes [M = Fe(III), Ru(III), Os(III)] also undergo electrochemical reductions to the corresponding monoanions.[9]

Experimental Section

Preparation of Compounds.—$Ru(dbm)_3$,[10] $Ru(SacSac)_3$,[9] $Ru(bipy)_3(ClO_4)_2$,[11] $Os(acac)_3$,[12] $Os(SacSac)_3$,[9] and $Os(bipy)_3(ClO_4)_2$[13] were prepared by published methods. *cis*- and *trans*-$Ru(tfac)_3$ and -$Ru(bzac)_3$ were available from previous work,[8] and the general procedure used to prepare these complexes was applied to the synthesis of $Ru(tfbzac)_3$ and $Ru(dpm)_3$. Benzoyltrifluoroacetone[14] and dipivaloylmethane[15] were obtained by literature methods. **Ru(tfbzac)$_3$** appeared as red crystals, mp 171–173°. *Anal.* Calcd for $C_{30}H_{18}F_9O_6Ru$: C, 48.27; H, 2.43; F, 22.90. Found: C, 47.55; H, 2.46; F, 22.30. $Ru(dpm)_3$ appeared as solid crystals (sublimed), mp 220–223°. *Anal.* Calcd for $C_{33}H_{57}O_6Ru$: C, 60.90; H, 8.83. Found: C, 61.10; H, 8.79.

(Ph$_4$As)[Ru(hfac)$_3$].—$K_2[RuCl_5(H_2O)]$ (0.52 g, 1.38 mmol) and 0.48 g (4.1 mmol) of potassium bicarbonate were refluxed in 5.0 ml of hexafluoroacetylacetone for 3 days. Chloroform (15 ml) was added, the mixture was refluxed for another day, and the

---

[1] National Science Foundation Predoctoral Fellow, 1970–present.

[2] P. Zuman, "Substituent Effects in Organic Polarography," Plenum Press, New York, N. Y., 1967.

[3] D. A. Buckingham and A. M. Sargeson in "Chelating Agents and Metal Chelates," F. P. Dwyer and D. P. Mellor, Ed., Academic Press, New York, N. Y., 1964, Chapter 6, and references therein.

[4] A. A. Vlček, *Progr. Inorg. Chem.*, **5**, 211 (1963).

[5] C. K. Mann and K. K. Barnes, "Electrochemical Reactions in Nonaqueous Systems," Marcel Dekker, New York, N. Y., 1970, Chapter 13.

[6] (a) J. A. McCleverty, *Progr. Inorg. Chem.*, **10**, 48 (1968); (b) D. C. Olson, V. P. Mayweg, and G. N. Schrauzer, *J. Amer. Chem. Soc.*, **88**, 4876 (1966).

[7] The following ligand abbreviations are employed: acac, acetylacetonate; dpm, dipivaloylmethanide; bzac, benzoylacetonate; tfac, trifluoroacetylacetonate; hfac, hexafluoroacetylacetonate; tfbzac, benzoyltrifluoroacetonate; dbm, dibenzoylmethanide; SacSac, dithioacetylacetonate.

[8] J. G. Gordon, II, M. J. O'Connor, and R. H. Holm, *Inorg. Chim. Acta*, **5**, 381 (1971).

[9] G. A. Heath and R. L. Martin, *Aust. J. Chem.*, **23**, 1721 (1970); A. M. Bond, G. A. Heath, and R. L. Martin, *J. Electrochem. Soc.*, **117**, 1362 (1970).

[10] L. Wolf, E. Butter, and H. Weinelt, *Z. Anorg. Allg. Chem.*, **306**, 87 (1960).

[11] F. H. Burstall, *J. Chem. Soc.*, 173 (1936).

[12] F. P. Dwyer and A. Sargeson, *J. Amer. Chem. Soc.*, **77**, 1285 (1955).

[13] F. H. Burstall, F. P. Dwyer, and E. C. Gyarfas, *J. Chem. Soc.*, 953 (1950).

[14] J. C. Reid and M. Calvin, *J. Amer. Chem. Soc.*, **72**, 2948 (1950).

[15] G. S. Hammond, D. C. Nonhebel, and C.-H. S. Wu, *Inorg. Chem.*, **2**, 73 (1963).

solid collected by filtration was washed thoroughly with chloroform and ethanol to remove red $Ru(hfac)_3$ and purple $K[Ru(hfac)_3]$, respectively. The chloroform washings were combined with the original filtrate and volatile components were removed, leaving an oily red material. This was dissolved in *ca.* 100 ml of ethanol containing 1.3 g (1.4 mmol) of potassium iodide (in order to reduce $Ru(hfac)_3$ to $Ru(hfac)_3^-$) and this solution was combined with the ethanol washings. Treatment with a concentrated aqueous solution of tetraphenylarsonium chloride followed by the addition of water as necessary effected precipitation of the crude salt. This material was purified by recrystallization from dichloromethane–*n*-heptane and the pure product was obtained as purple crystals in a yield of *ca.* 25%. The tetra-*n*-butylammonium salt was obtained by an analogous procedure and was recrystallized from carbon tetrachloride (pmr, acetone-d_6: CH 6.23 ppm downfield of TMS). *Anal.* Calcd for $C_{39}H_{23}AsF_{18}O_6Ru$: C, 42.37; H, 2.10; F, 30.93. Found: C, 41.83; H, 2.08; F, 30.87.

Ru(hfac)$_3$.—Either of the salts of $Ru(hfac)_3^-$ could be oxidized to $Ru(hfac)_3$ by reaction with 1.0 equiv of the one-electron oxidant $Ni[S_2C_2(CF_3)_2]_2$[16] in dry dichloromethane at room temperature. After removal of solvent, sublimation of the residue afforded a pure product as dark red crystals in 50–60% yield. *Anal.* Calcd for $C_{15}H_3F_{18}O_6Ru$: C, 24.95; H, 0.42; F, 47.35. Found: C, 24.71; H, 0.68; F, 47.85. A previously published preparation[17] gave low and erratic yields in our hands. The mixed-ligand complexes $Ru(acac)_2(hfac)$ and $Ru(acac)(hfac)_2$ were prepared by refluxing $Ru(hfac)_3$ and acetylacetone or $Ru(acac)_3$ in toluene for at least 7 days. The solvent was removed *in vacuo* and the residue was used in the polarographic experiments without further purification.

Polarographic Measurements.—A Princeton Applied Research Model 170 electrochemistry system was employed. The usual polarographic measurements were carried out using a rotating platinum electrode; the platinum electrode for cyclic voltammetry has been described previously.[18] All potentials were determined at 25.0 ± 0.1° *vs.* sce. Cyclic voltammetric current–potential curves obtained at scan rates of 0.002–0.5 V/sec were plotted by an X-Y recorder and those at faster scan rates up to 100 V/sec were displayed on a Tektronix storage oscilloscope. DMF was purified by vacuum distillation from anhydrous copper sulfate and acetonitrile was purified by a literature method.[19] Solutions were *ca.* 1–2 m*M* in complex and 0.10 *M* in tetraethylammonium perchlorate as supporting electrolyte.

Results and Discussion

Ruthenium complexes are particularly suitable for electrochemical studies because of the existence of two well-defined oxidation states (II, III) of the metal ion, the kinetic stability of each,[20] as evidenced, *e.g.*, by the retention of enantiomeric[21] and geometrical[8] configurations in the redox cycle Ru(II) → Ru(III) → Ru(II), and the small structural differences between octahedral Ru(II,III) complexes,[22] which promote rapid and reversible electron transfer. Recent work has shown that both oxidation states can be stabilized in bi- and polynuclear complexes[23] and that various total oxidation levels of such species are detectable by voltammetric measurements. In accordance with these expectations ruthenium tris(β-diketonates) exhibited uncomplicated polarographic behavior in DMF or acetonitrile solution with current–voltage curves indicative of reversible or near-reversible one-electron-transfer reactions, $Ru(R_1COCHCOR_2)_3 + e^- \rightleftharpoons Ru(R_1COCHCOR_2)_3^-$, and half-wave potentials very strongly influenced by the nature of the chelate ring substituents R_1 and R_2. Polarographic data are collected in Table I. Reversibility of the electrode reaction has been investigated in several ways. In nearly all cases the slope of the plot of E *vs.* $\log [(i_d - i)/i]$ did not deviate more than 2–3 mV from the value of 59 mV expected for a reversible couple. The typical complexes $Ru(acac)_3$ and $Ru(tfbzac)_3$ were additionally investigated by cyclic voltammetry. Plots of $i_p/v^{1/2}$ and $i_{p,c}/i_{p,a}$ *vs.* v were linear in the range 0.01–10 V/sec,[24] consistent with reversible electron transfer[25] within this interval. $Ru(hfac)_3$ and two salts of $Ru(hfac)_3^-$ were prepared. Polarograms in acetonitrile yielded identical half-wave potentials.

TABLE I
POLAROGRAPHIC DATA FOR RUTHENIUM AND OSMIUM COMPLEXES IN DMF SOLUTION[a] AT 25°

No.	Complex	$E_{1/2}$, V[b]	Slope, mV
1	$Ru(dpm)_3$	−1.038	56
2	$Ru(acac)_3$	−0.728	61
3, 4[c]	$Ru(bzac)_3$	−0.593	59
5	$Ru(dbm)_3$	−0.501	56
6	$Ru(acac)_2(hfac)$	−0.184	*e*
7, 8[c]	$Ru(tfac)_3$	−0.016	60
9	$Ru(tfbzac)_3$	+0.104	59
10	$Ru(acac)(hfac)_2$	+0.332	68
11	$(Ph_4As)[Ru(hfac)_3]$	+0.804	62
	$(n\text{-}Bu_4N)[Ru(hfac)_3]$[d]	+0.726	60
	$Ru(hfac)_3$[d]	+0.726	68
	$Os(acac)_3$	−1.244	58
	$Ru(SacSac)_3$	−0.010	56
	$Os(SacSac)_3$	−0.151	62
	$Ru(bipy)_3(ClO_4)_2$	+1.282	68
	$Os(bipy)_3(ClO_4)_2$	+0.828	68

[a] Acetonitrile solutions used where indicated. [b] ±0.005 V. Where checked potentials obtained with a dme agreed to within ±0.010 V of those obtained at the rpe. [c] Cis and trans isomers. [d] Acetonitrile. $Ru(hfac)_3$ is unstable to reduction in DMF. [e] Not determined due to the small concentration of the products of the ligand-exchange reaction.

Inspection of these data in Table I immediately reveals the qualitative behavior of the half-wave potentials with the nature of the substituent. Potentials become more positive (increasing ease of reduction of the Ru(III) species) as the number and type of electron-releasing substituents are decreased. Because these complexes can be assumed to possess similar trigonal geometries and a common redox-active center, the mechanism of electron transfer at the electrode should be the same, and, as with related series of organic molecules,[2] linear free energy relationships may be sought. Plots of $E_{1/2}$ (or $\Delta E_{1/2}$ with $E_{1/2}(Ru(acac)_3) = 0$) *vs.* appropriate sums of Hammett (σ_m, σ_p) or Taft (σ^*) constants[2,26] reveal the following linear relationships: $E_{1/2}(V) = 0.381\Sigma\sigma_p - 0.448$, $0.548\Sigma\sigma_m - 0.605$, $0.267\Sigma\sigma^* - 0.689$ (least-squares fits). A

---

(16) A. Davison, N. Edelstein, R. H. Holm, and A. H. Maki, *Inorg. Chem.*, **2**, 1227 (1963).

(17) H. Veening, W. E. Bachman, and D. M. Wilkinson, *J. Gas Chromatogr.*, **5**, 248 (1967).

(18) C. E. Forbes, A. Gold, and R. H. Holm, *Inorg. Chem.*, **10**, 2479 (1971).

(19) J. F. O'Donnell, J. T. Ayres, and C. K. Mann, *Anal. Chem.*, **37**, 1161 (1965).

(20) (a) H. Taube in "Survey of Progress in Chemistry," to be published; (b) P. C. Ford, *Coord. Chem. Rev.*, **5**, 75 (1970).

(21) H. Elsbernd and J. K. Beattie, *Inorg. Chem.*, **8**, 983 (1969).

(22) H. C. Stynes and J. A. Ibers, *ibid.*, **10**, 2304 (1971).

(23) (a) C. Creutz and H. Taube, *J. Amer. Chem. Soc.*, **91**, 3988 (1969); (b) S. A. Adeyemi, J. N. Braddock, G. M. Brown, J. A. Ferguson, F. J. Miller, and T. J. Meyer, *ibid.*, **94**, 300 (1972).

(24) For the $Ru(acac)_3$ couple the mean values of $i_p/v^{1/2}$ and $i_{p,c}/i_{p,a}$ over the range of 0.01–10 V/sec were 26.7 (0.6) $\mu A\ sec^{1/2}\ V^{-1/2}$ and 0.98 (0.01) respectively, where the numbers in parentheses are mean deviations. Corresponding values for the $Ru(tfbzac)_3$ couple were 24.7 (0.7) $\mu A\ sec^{1/2}\ V^{-1/2}$ and 0.99 (0.02) over the same range. (v is the scan rate in V/sec, $i_{p,c}$ the cathodic peak current, and $i_{p,a}$ the anodic peak current.)

(25) R. S. Nicholson and I. Shain, *Anal. Chem.*, **36**, 706 (1964).

(26) K. B. Wiberg, "Physical Organic Chemistry," Wiley, New York, N. Y., 1964, pp 410–411.

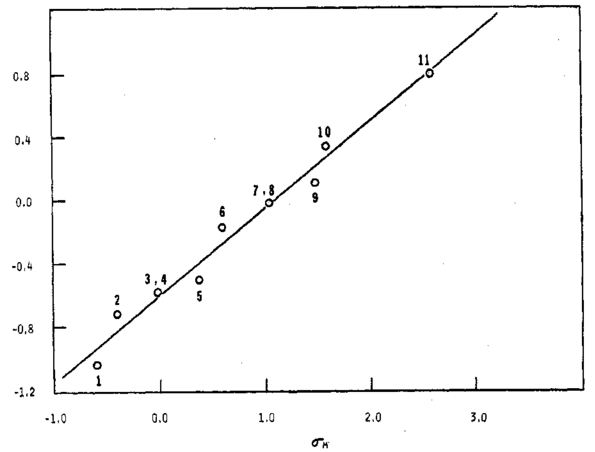

Figure 1.—Plot of half-wave potential *vs.* sum of Hammett substituent constants σ_m for tris(β-diketonato) ruthenium(II,III) complexes in DMF solution. Complexes are numbered as in Table I.

plot of the second equation is shown in Figure 1. Free energy relationships of this sort have been little tested and lack firm theoretical justification for metal complexes. For the present series of complexes they are best regarded as empirical analytical expressions of substituent effects on the $Ru(R_1COCHCOR_2)_3 \rightleftharpoons Ru(R_1COCHCOR_2)_3^-$ redox couples.

The substituent effects are extremely pronounced and for the limiting cases, $Ru(dpm)_3$ and $Ru(hfac)_3$, define a potential interval of 1.84 V in DMF, which appears to be the largest such interval yet found for redox reactions of a series of substituted metal complexes containing a common structural core. Previously, potential intervals of *ca.* 1.2–1.5 V have been observed for the $z = 2- \rightleftharpoons z = 1- \rightleftharpoons z = 0$ processes of bis- and tris(dithiolene) complexes[6] $M(S_2C_2R_2)_{2,3}^z$ (not including M = Ru), whose delocalized electronic structures are well recognized and for which $\Delta E_{1/2}$–$\Sigma\sigma^*$ linear correlations have been found.[6b] Adopting a qualitative one-electron picture for the present series of complexes, it is concluded that the MO describing electrons added or subtracted in the redox process must possess appreciable ligand character. These electrons may be reasonably associated with the configurations $t_{2g}^{5,6}$ in octahedral microsymmetry or $a_1^2e_a^{3,4}$ in trigonal symmetry.[27] Inasmuch as the t_{2g} (e_a) metal orbitals can mix with π ($\sigma + \pi$) ligand MO's and variation of substituents will necessarily alter the energies of both types of ligand orbitals,[28] some degree of substituent dependence of $E_{1/2}$ is expected,[29] particularly for reversible processes. The importance of the relatively large radial extension of octahedral Ru(II) $d\pi$ orbitals has recently been emphasized by Taube.[20a] Concerning other data in Table I, it is seen that $Os(acac)_3$ is more difficult to reduce than $Ru(acac)_3$ (by 0.52 V), in keeping with the usual behavior of Os(III) and Ru(III), and that a much smaller difference (0.14 V[30]) exists between the half-wave potentials of $Ru(SacSac)_3$ and $Os(SacSac)_3$. The latter result may imply a larger and/or more nearly constant ligand character of the t_{2g} (or e_a) orbital.

The majority of redox potentials reported for other ruthenium complexes were obtained from cell measurements;[3,20,31] only a limited number of half-wave potentials have been previously determined.[32] In order to provide an approximate relationship between the potentials in Table I and the standard reduction potentials of Ru(II,III) complexes in aqueous solution, the voltammetry of $Ru(bipy)_3^{2+}$ and $Os(bipy)_3^{2+}$ in DMF was investigated. One-electron waves, whose slopes and cyclic voltammetric characteristics indicated quasireversible behavior, were found with $E_{1/2}$ values *ca.* 0.2 V higher than their $E°$ values[3] corrected to sce reference. This value is a rough empirical estimate of the potential difference due to different solvents, liquid junction potentials, ionic strength, and other factors. Some representative $E°$(sce) values (in volts) for aqueous couples are the following: $Ru(H_2O)^{3+,2+}$, +0.01; $Ru(NH_3)_6^{3+,2+}$, −0.14; $Ru(en)_3^{3+,2+}$, −0.03; $Ru(CN)_6^{3-,4-}$, +0.62; $Ru(bipy)_3^{3+,2+}$, +1.06. Using these data as a guide it is seen that, in their respective media, the following species as examples have roughly comparable oxidizing power: $Ru(tfac)_3$–$Ru(NH_3)_6^{3+}$, $Ru(tfbzac)_3$–$Ru(en)_3^{3+}$, and $Ru(hfac)_3$–$Ru(CN)_6^{3-}$. The large positive half-wave potential of $Ru(hfac)_3$ suggests its use as a specific one-electron oxidant in nonpolar solvents, analogous to the reactions of the neutral dithiolenes $M[S_2C_2(CF_3)_2]_{2,3}$, whose potentials are similar (*ca.* +0.8 to +1.1 V[6a]).

Electrochemical evidence has also been obtained for the existence of ruthenium(IV) β-diketonates. Anodic polarograms of the following complexes in DMF have yielded quasireversible one-electron waves with the indicated $E_{1/2}$ values (volts): $Ru(dpm)_3$, +0.92; $Ru(acac)_3$, +1.07; $Ru(bzac)_3$, +1.05; $Ru(hfac)_3$, +1.06. In contrast to earlier results these potentials show a slight substituent dependence, and their high positive values suggest that uncomplicated chemical oxidation might be difficult to achieve. In seeking more stable Ru(IV) species the voltammetry of the dithiocarbamate complex $Ru(Et_2(dtc))_3$ has been examined. The complex undergoes a nearly reversible one-electron reduction ($E_{1/2}$ = −0.741 V) and a one-electron oxidation at +0.382 V in DMF,[33] indicating that $Ru(Et_2(dtc))_3^+$ should be synthetically accessible. The corresponding Fe(IV) cations, including $Fe(Et_2(dtc))_3^+$, have recently been prepared.[34] Voltammetry of the precursor $Fe(Et_2(dtc))_3$ in DMF reveals a one-electron reduction at −0.447 V and a reversible one-electron oxidation at a potential (+0.423 V) only slightly different from that of its ruthenium analog. As the results cited by Pasek and Straub[34] indicate, stabilization of the IV oxidation state in tris(dithiocarbamates) may be of some general occurrence. Consistent with this possibility we find that

---

[27] A. K. Gregson and S. Mitra, *Chem. Phys. Lett.*, **3**, 392 (1969).

[28] K. DeArmand and L. S. Forster, *Spectrochim. Acta*, **19**, 1393 (1963).

[29] Due to the lack of information for a similarly extensive series of tris(β-diketonates) of other metal ions, it cannot be argued at present that the potential interval found for the ruthenium complexes is exceptionally large. Electrochemical studies of other d⁵ and d⁶ complexes such as $M(acac)_3$ [M = Fe(III), Co(III), Rh(III)] and $M(hfac)_3$ [M = Co(III), Rh(III)], as well as the analogous Cr(III) complexes, yielded irreversible waves and were not pursued in detail.

[30] A difference of 0.09 V has been observed in acetone solution.[9]

[31] D. D. DeFord and A. W. Davidson, *J. Amer. Chem. Soc.*, **73**, 1469 (1951); T. J. Meyer and H. Taube, *Inorg. Chem.*, **7**, 2369 (1968); E. E. Mercer and R. R. Buckley, *J. Phys. Chem.*, **70**, 3103 (1966).

[32] I. J. Itzkovitch and J. A. Page, *Can. J. Chem.*, **46**, 2743 (1968); P. E. Dumas and E. E. Mercer, *Inorg. Chem.*, **11**, 531 (1972).

[33] A further two-electron oxidation ($E_{1/2}$ = +1.29 V) has also been observed.

[34] E. A. Pasek and D. K. Straub, *Inorg. Chem.*, **11**, 259 (1972).

$Co(Et_2(dtc))_3$ undergoes a one-electron oxidation at +0.949 V in addition to a similar but irreversible reduction at −1.07 V in DMF. Lastly, it is noted that the complexes $M(R_1R_2(dtc))_2(S_2C_2R_2)^z$ [35] (M = Fe, Ru; R = CF_3, CN) exist as a four-membered electron-transfer series (z = 2−, 1−, 0, 1+). The stabilization of M(IV) in either of the two highest oxidation levels is currently under investigation.[36]

Acknowledgments.—This research was supported by the National Science Foundation under Grant GP-18978X. We thank Professor H. Taube for a copy of ref 20a prior to its publication.

---

[35] L. H. Pignolet, R. A. Lewis, and R. H. Holm, *J. Amer. Chem. Soc.*, **93**, 360 (1971); *Inorg. Chem.*, **11**, 99 (1972).

[36] L. H. Pignolet, R. A. Lewis, J. F. Weiher, G. S. Patterson, and R. H. Holm, unpublished work.

Correspondence

Copper(I) Complexes of 1,8-Naphthyridine

Sir:

Recently it was reported[1] in this journal that cupric perchlorate forms a tris complex with 2,7-dimethyl-1,8-naphthyridine (dmNN) having the formula $Cu(dmNN)_3(ClO_4)_2$ (A). Analytical data, a uv spectrum and a partial list of infrared spectral bands were given in the paper. No magnetic data were reported. The color of the compound was described as brown.

An attempt was made in this laboratory to duplicate this synthesis using the parent 1,8-naphthyridine (NN) instead of dmNN. The initial attempts failed, but by varying the described conditions of the reaction, an orange compound B was obtained. This compound proved on elemental analysis to be a copper(I) perchlorate complex of NN. It was diamagnetic, and spectra of solutions in acetonitrile and nitromethane showed no bands in the region 8000–15,000 cm^{-1} in which copper(II) usually absorbs.

As a result of this experience, a sample of 2,7-dimethyl-1,8-naphthyridine was prepared and the synthesis reported in ref 1 was duplicated exactly. The reaction proceeds just as described and yields a brown product (A′), but elemental analysis indicated this compound is also a complex of copper(I) perchlorate. The complex A′ is identical with A, prepared by Hendricker and Bodner. A′ was prepared exactly as Hendricker and Bodner described the preparation of A, and the two compounds have identical ir and uv spectra.

In Table I the theoretical percentages of C, H, N, Cu, and ClO_4^- are given for the formula proposed here and for that proposed by Hendricker and Bodner.

TABLE I

THEORETICAL PERCENTAGES FOR TWO POSSIBLE COPPER PERCHLORATE COMPLEXES

Compd formula	% C	% H	% N	% Cu	% ClO_4^-
$Cu(C_{10}H_{10}N_2)_3(ClO_4)_2$ (A)	48.89	4.10	11.40	8.62	26.99
$Cu(C_{10}H_{10}N_2)_2ClO_4$ (A′)	50.11	4.21	11.69	13.25	20.75

As can be seen from this comparison, C, H, and N analyses are very similar for the two compositions. Copper and perchlorate percentages are very different. Hendricker and Bodner listed only C, H, and N analyses in their paper, so their data are not suitable for distinguishing the two possible formulas. The analyses given below clearly establish this compound as the copper(I) complex $Cu(C_{10}H_{10}N_2)_2ClO_4$.

Since in both of these preparations a copper(I) complex results from a copper(II) starting material, some unexpected reducing agent must be present. This agent appears to be an impurity in the drying agent 2,2′-dimethoxypropane (DMP).

When previously dried starting materials are used and DMP is omitted from the reaction mixture, the copper(I) perchlorate complexes did not form. When a freshly opened bottle of DMP was used instead of a previously opened one, the yield of product was severely reduced. These two observations suggest that some decomposition product of the dimethoxypropane is oxidized by the copper. Ethers are well known to decompose on standing to give a variety of unstable peroxides. Kochi and Mains[2] have investigated the reactions of a number of copper salts with free radicals derived from organic peroxides and found that reduction of copper(II) by these species occurs readily. It therefore seems likely that peroxides arising from slow decomposition of the DMP are responsible for the reduction of copper in this reaction.

The ready preparation of these copper(I) perchlorates suggested that one might be able to prepare other complexes of NN and dmNN directly from copper(I) salts. The brown microcrystalline compounds $Cu_2(NN)Cl_2$ and $Cu_2(dmNN)Cl_2$ have been prepared and characterized as described below.

Preparations. Cu(1,8-naphthyridine)ClO_4 (B).—To a solution of 0.1 g of $Cu(NN)_4(ClO_4)_2$ in 30 ml of absolute methanol, 10 ml of 2,2′-dimethoxypropane was added. The solution was refluxed for 4 hr and then 0.3 g of cupric perchlorate hexahydrate was added. After refluxing for 12 hr more the solution was concentrated by warming under reduced pressure to half its original volume and then placed in a desiccator under nitrogen and over sodium hydroxide. The orange crystals were collected by filtration, washed with chloroform, and dried over calcium chloride. The compound was recrystallized from nitromethane. *Anal.* Calcd for $Cu(C_8H_6N_2)ClO_4$: Cu, 21.67; C, 32.78; H, 2.06. Found: Cu, 21.36; C, 32.67; H, 2.00.

---

[1] D. G. Hendricker and R. L. Bodner, *Inorg. Chem.*, **9**, 273 (1970).

[2] J. K. Kochi and H. E. Mains, *J. Org. Chem.*, **30**, 1862 (1965).