of this rotatory strength arises from tyrosine 92, which contributes 0.56 DM ($\epsilon = 2$). However, a portion of this apparently arises from exciton interactions with tyrosines 25 and 97, which contribute rotatory strengths of −0.20 and −0.16 DM, respectively. All other ^1L_a transitions develop rotatory strengths at least an order of magnitude lower.

It is difficult to make definite assignments as to which residues are interacting with tyrosine 92, since all the states are mixed in the Hamiltonian matrix. However, one can obtain an idea as to the importance of certain interactions from the magnitude of the off-diagonal elements of the secular equation. On this basis, it appears that tyrosine 92 is interacting to a significant extent with the peptide transitions of residues 25 through 33, tyrosine 97, and its own peptide transition. However, it must be remembered that these off-diagonal terms of the secular equation are only interaction energies, so a large value for an off-diagonal term does not necessarily indicate a large contribution to the rotatory strength.

In any event, it is obvious that we can calculate sufficient rotatory strength from the ^1L_a bands of the tyrosine residues of RNase S to account for the experimentally observed region of positive ellipticity near 240 nm. In fact, as is apparent from Figure 1, the mean residue ellipticity in this region of the spectrum is grossly overestimated. There are several factors which could be responsible for this. The spectrum was calculated for a perfectly rigid conformation, whereas there certainly must be vibrational oscillations present in the real molecule which would be expected to diminish the intensity of the band. Furthermore, as was indicated above, the bandwidth of the ^1L_b transitions which was used to compute the theoretical curves was probably too small. Since the Cotton effects of the ^1L_b and ^1L_a bands are of opposite signs, a wider bandwidth for ^1L_b would reduce the magnitude of the ellipticity in the 240-nm region. In fact, if the bandwidths are regarded as adjustable parameters, the calculated curves can be brought into much better agreement with experiment. However, the most significant factor in the present case is simply that the rotatory strengths of the peptide n-π^* transitions have been seriously underestimated.

We have not really given much attention to the peptide bands. In fact, the peptide bands were originally included in the calculation simply to produce the required red shift of the ^1L_a band. However, the ellipticity calculated for the π-π^* region near 210 nm, with a dielectric constant of unity, appears to agree reasonably well with the experimental spectrum. Nevertheless, our calculation seriously underestimates the rotatory strength which should arise from the n-π^* transitions. Underestimation of the n-π^* rotatory strength is a problem which is common to other theories of the optical activity of polypeptides.[10] However, the discrepancy is even greater in the present case. This appears to be a property of the coordinate set which was used for these calculations. Preliminary calculations, which were carried out with RNase S coordinate set 2 (map 20) gave much larger rotatory strengths for the n-π^* transitions, in good quantitative agreement with the results reported by Madison and Schellman.[10] The origin of this difference is currently under investigation.

In conclusion, it appears that the region of positive ellipticity, which can be observed near 240 nm in the CD spectra of RNase S, definitely includes major contributions from the ^1L_a transitions of the tyrosine residues, especially from tyrosine 92. It is possible that other chromophoric groups might make contributions in this region. For example, the cystine residues could give rise to large rotatory strengths. However, the rotatory strengths which are calculated for the tyrosines are certainly sufficient to account for the effect.

The positive CD band near 240 nm might be somewhat weaker in RNase S than in RNase A.[2,4] This difference may be associated with a conformational difference in the vicinity of tyrosine 92. A more detailed investigation of the differences in the CD spectra of RNase A and RNase S is planned.

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Detection and Characterization of Radical Cations Produced by One-Electron Chemical and Electrochemical Oxidations of Organocobalt Compounds

Sir:

We wish to report the direct detection and characterization of radical cations produced by one-electron oxidation of organocobalt(III) compounds.

The study of the chemical and electrochemical *reduction* of organocobalt compounds has received considerable attention, particularly in the context of the chemistry of vitamin B_{12} derivatives and models.[1-4] In contrast, the corresponding *oxidation* processes have not thus far been extensively investigated and are poorly characterized. Studies on the oxidative cleavage of benzylaquobis(dimethylglyoximato)cobalt(III) provide indirect evidence for transient one-electron oxidation products (*formally* organocobalt(IV) species)[5-7] as do brief reports of electrochemical studies on organocobalt Schiff's base complexes.[4,8] We now report the direct detection and characterization of such species.

Spectral titrations at −78° of acidic aqueous methanol solutions (80 vol % methanol) of various organobis(dimethylglyoximato)cobalt(III) complexes ($[RCo(DH)_2(H_2O)]$, abbreviated [CoR] where R = alkyl or benzyl) with cerium(IV) nitrate demonstrated the occurrence of a stoichiometric 1:1 reaction, in accord with eq 1.

$$[RCo(DH)_2(H_2O)] + Ce(IV) \longrightarrow [RCo(DH)_2(H_2O)]^+ + Ce(III) \quad (1)$$

Table I. Results of Cyclic Voltammetry Measurements on $[\text{RCo(DH)}_2(\text{H}_2\text{O})]$ and EPR Measurements on $[\text{RCo(DH)}_2(\text{H}_2\text{O})]^+$

R	$E_{1/2}$, V vs. SCE[a]	g (±0.001)	$\langle A_{\text{Co}}\rangle$, G (±0.5)
CH_3	0.902	2.021	28.8
C_2H_5	0.878	2.026	31.7
n-C_3H_7	0.867	2.027	32.0
i-C_3H_7	0.856	2.033	34.8
p-$NO_2C_6H_4CH_2$	0.907	2.020	28.6
p-$ClC_6H_4CH_2$	0.876	2.026	30.4
p-$FC_6H_4CH_2$	0.873	2.028	30.9
$C_6H_5CH_2$	0.859	2.029	31.3
p-$CH_3C_6H_4CH_2$	0.849	2.030	31.1
C_6H_5		2.012	24.5

[a] $E_{1/2} = {}^1/_2(E_a + E_c)$ measured in 1.0 M $HClO_4$ at scan rates ranging from 1 to 100 V/sec. Estimated accuracy ±0.002 V.

Solutions of $[\text{RCo(DH)}_2(\text{H}_2\text{O})]^+$ (10^{-4} to 10^{-3} M) prepared in this way, which were stable for many hours at $-78°$, absorbed throughout the visible-uv region, a typical spectrum (for R = C_2H_5) having an absorption maximum at 400 nm ($\epsilon \sim 3 \times 10^3$ M^{-1} cm^{-1}) and shoulders at 450 and 525 nm ($\epsilon \sim 2.5 \times 10^3$ and 1.5×10^3, respectively).

At $-196°$, frozen solutions prepared as above, exhibited well-defined EPR spectra consisting of eight relatively broad ($\sim$20 G) but well-resolved lines reflecting coupling of the unpaired electron with the nuclear spin of ^{59}Co ($I = 7/2$) with no detectable ligand (e.g., ^{14}N) hyperfine splitting. Although a slight anisotropy was evident, the resolution was insufficient to permit evaluation of both the parallel and perpendicular components and only a single g value (computed from the mean position (relative to DPPH) of the $m_I = 7/2$ and $m_I = -7/2$ hyperfine component lines) and a single A value (computed from the separation of these two lines) could be determined. The range of these values listed in Table I for several alkyl- and benzyl-cobalt compounds, was found to be g = 2.012 to 2.033 and $\langle A_{\text{Co}}\rangle$ = 24.5–31.3 G. While demonstrating that some unpaired electron density is localized on the Co atom, these data provide little detailed information about the electron distribution and leave open the question of the degree to which the electronic structures of these radical cations departs from their limiting formal representation as d^5 cobalt(IV) complexes, through ligand-to-cobalt charge transfer contributions from structures such as $[\text{Co}^{\text{III}}\text{-R}\cdot]$. It is hoped that refinement of the EPR measurements, including the extension of such measurements to liquid solutions, will throw further light on these themes.[9]

Warming a solution of $[\text{CoR}]^+$ (R = C_2H_5), prepared as above, to ca. $-20°$ resulted in decomposition within a few hours with the re-formation of the organocobalt(III) complex, [CoR], to the extent of 50% of the original concentration of $[\text{CoR}]^+$. The kinetics of this decomposition were approximately *second-order* in $[\text{CoR}]^+$ and the rate was markedly suppressed by the addition of [CoR]. These results are in accord with the following decomposition scheme and provide additional support for the proposed identity of $[\text{CoR}]^+$ as being derived from [CoR] by simple one-electron oxidation, *without decomposition*, since it readily reverts to [CoR].

$$2[\text{CoR}]^+ \rightleftharpoons [\text{CoR}] + [\text{CoR}]^{2+} \text{ (reversible)} \qquad (2)$$

$$[\text{CoR}]^{2+} \longrightarrow \text{decomposition products} \qquad (3)$$

The reversible disproportionation of $[\text{CoR}]^+$ according to eq 2 is analogous to the corresponding reaction recently reported for the electrochemically generated $[\text{Cr(CO)}_6]^+$ radical cation.[10] The probable products of decomposition of $[\text{CoR}]^{2+}$ are Co(III) and ROH, although this remains to be confirmed. Suppression of the above decomposition mode by addition of [CoR] revealed a slow residual ***first-order*** decomposition reaction of $[\text{CoR}]^+$, with a half-life of ca. 2×10^4 sec at $-20°$ (presumably corresponding to the first-order room temperature decomposition process, discussed below).

Evidence for the reversible one-electron oxidations of various $[\text{RCo(DH)}_2\text{H}_2\text{O}]$ complexes ***in aqueous solution at room temperature*** was also obtained from electrochemical measurements similar to those reported by Costa[4] and by Vol'pin[8] for related Schiff's base complexes. Cyclic voltammetry measurements on a series of such complexes using a platinum electrode, with scan rates ranging from 1 to 100 V/sec, yielded voltammograms characteristic of reversible one-electron oxidation processes ($E_c - E_a = 60 \pm 10$ mV, n = 1.0), from which the reversible oxidation potentials, $E_{1/2}$, listed in Table I were determined. The trend of $E_{1/2}$ values as R is varied parallels that for the rates of oxidation of [CoR] by IrCl_6^{2-} (interpreted as an outer sphere one-electron transfer process)[5,11] and is in the expected direction of increasing ease of oxidation of CoR with increasing electron donor power of R. From the reversibility of the cyclic voltammograms it could be deduced that the lifetimes of the $[\text{CoR}]^+$ radical cations decreased in the order R = CH_3, C_2H_5 > i-C_3H_7 and p-$NO_2C_6H_4CH_2$ > $C_6H_5CH_2$ ≫ p-$CH_3OC_6H_4CH_2$ (oxidation of the latter organocobalt compound being irreversible at scan rates as high as 100 V/sec). This is consistent with a decomposition mode involving nucleophilic attack on R (and leading to the typical products under these conditions, Co(II) and ROH) as is the observation that the lifetime of $[\text{CoR}]^+$ is reduced by addition of nucleophiles such as Cl^-.

In a few cases (notably for R = CH_3, C_2H_5, and n-C_3H_7) the lifetime of $[\text{CoR}]^+$ was sufficiently long (ca. 1 min) that aqueous solutions of $[\text{CoR}]^+$, sufficiently stable for characterization of the latter, could be prepared at room temperature by oxidizing [CoR] chemically (with Ce(IV)) or electrochemically (using a Pt mesh electrode). The spectrum of the transient $[n\text{-C}_3\text{H}_7\text{Co(DH)}_2(\text{H}_2\text{O})]^+$ ion in aqueous solution at 25°, determined in stopped-flow experiments using Ce(IV) as oxidant, was similar to that of the corresponding stable $[\text{CoR}]^+$ ion in methanol at $-78°$, confirming that the same species is formed under both conditions. These experiments also yielded direct measurements of the rate of decomposition of $[\text{CoR}]^+$ which, in aqueous solution at 25°, obeyed first-order kinetics ($k \sim 9 \times 10^{-3}$ sec^{-1} for R = n-C_3H_7). Presumably, the second-order decomposition mode which predominates at lower temperatures, i.e., at ca. $-20°$ in methanol, is favored under the latter conditions because of the lower activation energy of the disproportionative electron trnsfer process (eq 2) compared with the first-order solvent-induced decomposition.

Finally, we have confirmed our earlier suggestion[5] that the oxidation of CoR by IrCl_6^{2-} involves an initial one-electron transfer, by establishing for several cases (i.e., R = $C_6H_5CH_2$, n-C_3H_7, and i-C_3H_7) that the complete rate law conforms to eq 4 which is derived for the stepwise mechanism depicted by eq 5 and 6.[12]

$$\frac{-d[\text{CoR}]}{dt} = \frac{k_5k_6[\text{CoR}][\text{IrCl}_6^{2-}]}{k_{-5}[\text{IrCl}_6^{3-}] + k_6} \qquad (4)$$

$$[\text{CoR}] + \text{IrCl}_6^{2-} \underset{k_{-5}}{\overset{k_5}{\rightleftharpoons}} [\text{CoR}]^+ + \text{IrCl}_6^{3-} \qquad (5)$$

$$[\text{CoR}]^+ + \text{H}_2\text{O} \xrightarrow{k_6} \text{Co(II)} + \text{ROH} \qquad (6)$$

For R = n-C_3H_7, kinetic measurements[13] yielded the values $k_5 = 1.3$ M^{-1} sec^{-1} and $k_{-5}/k_6 = 5.5$ M^{-1}. Combination with the electrochemically determined[14] equilibrium quotient K_5 (= k_5/k_{-5} = 1.9×10^{-3}) yields k_6 = 7.4×10^{-3} sec^{-1}, in satisfactory agreement with the value of 9.2×10^{-3} sec^{-1} derived from direct measurements of the rate of decomposition of $[n\text{-}C_3H_7Co(DH)_2(H_2O)]^+$ as described above.

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(13) These measurements encompassed the initial concentration ranges 2×10^{-2} to 8×10^{-3} *M* CoR, 3.7×10^{-5} to 7.5×10^{-4} *M* $IrCl_6^{2-}$, and 0 to 3.1×10^{-3} *M* $IrCl_6^{3-}$, all at 25° and 1 *M* $HClO_4$.
(14) Log $K_5 = [E_{1/2}(IrCl_6^{3-}) - E_{1/2}(CoR)]/0.059$.
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A New 1,2-Rearrangement of Carbon from Sulfur to Carbon in Allyl and Benzyl Dithiocarbamates

Sir:

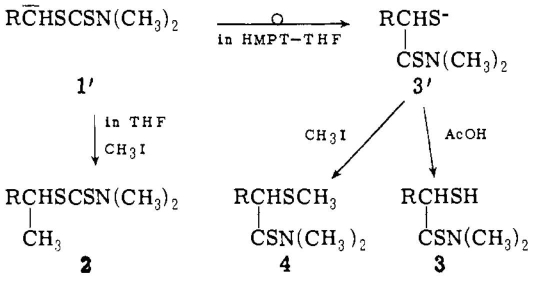
A 1,2-rearrangement of an ether to its isomeric alcohol which can occur upon metalation with excess organolithium reagent is well known as the Wittig rearrangement.[1,2] Here migration of carbon from sulfur to a negatively charged carbon occurs. However, rearrangement of this type has not been reported for sulfur analogs, except for the case in which silicon is the migrating atom.[3,4] In general, metalation of the rather acidic proton flanked by sulfur in sulfides,[5] sulfoxides,[6] and sulfones[7] produces stable carbanions which do not rearrange.

We now report the first example of a Wittig type rearrangement, where migration of carbon from sulfur to an α-carbanion occurs.[8] β-Methallyl and benzyl *N*,*N*-dimethyldithiocarbamates (**1a** and **1b**) are quite readily metalated with a slight excess of lithium diisopropylamide in tetrahydrofuran(THF) at −60°. Treatment of the resulting carbanions (**1′**) with methyl iodide affords α-methyl-β-methallyl and α-methylbenzyl *N*,*N*-dimethyldithiocarbamates (**2a** and **2b**) in an excellent yield.[9] However, the reaction, when conducted in the presence of hexamethylphosphoric triamide (HMPT), takes a wholly different course to give *N*,*N*-dimethyl-2-methylthio-3-methylbut-3-enethioamide (**4a**) and phenylthioacetamide (**4b**) in a practically quantitative yield.

Table I. Reaction of 1 with CH_3I

Dithiocarbamate	Solvent HMPT–THF (w/w)	Reaction time (min)	Yield (%)	Product ratio (%) 4	2
1a	0:1	5	98	0	100
1a	1:5	10	84.8	50	50
1a	1:3	30	96.2	100	0
1a	1:2	10	87.2	86	14
1a	1:1	10	82	97.3	2.7
1b	0:1	5	99	0	100
1b	1:2	7	93	53	47
1b	1:1	60	96	100	0

In a typical experiment, 14 mmol of **1** was introduced at −60° to 15 mmol of lithium diisopropylamide in a mixture of 10 ml of *n*-hexane and 25 ml of HMPT–THF (1:3 (w/w)) during 5 min. A deep violet color developed at once. The solution was stirred at −60°, until the violet color disappeared. The resulting orange solution was quenched with methyl iodide or acetic acid, becoming pale yellow. Quenching with acetic acid yielded *N*,*N*-dimethyl-2-mercapto-3-methylbut-3-enethioamide (**3a**) or phenylthioacetamide (**3b**), a new class of compounds. After washing with water, evaporation of the solvent gave products **3** or **4** in a practically quantitative yield.



a, R = $CH_2{=}C(CH_3)$

b, R = C_6H_5

Elemental analysis and mass spectra showed that **3** and **4** are isomeric with **1** and **2,** respectively. Structures **2, 3,** and **4** were assigned by spectral studies: **2b,**[10] mp 42–43°; NMR ($CDCl_3$) δ 1.79 (t, *J* = 6.8 Hz, CH_3), 3.30 and 3.42 (s, broad, $(CH_3)_2N$), 5.26 (q, *J* = 6.8 Hz, CH), and 7.20–7.54 ppm (m, C_6H_5); ir (Nujol) 1140 cm ($\nu_{C=S}$); *m/e* 225 (M^+), 105 ($M^+ - SCSN(CH_3)_2$); **3a,** oil which solidified in a refrigerator and gradually decomposed on standing at room temperature, NMR ($CDCl_3$) δ 1.92 (s, $CH_3C{=}$), 2.95 (d, *J* = 7.6 Hz, SH), 3.40 and 3.56 (s, $(CH_3)_2N-$), 4.83 (d, *J* = 7.6 Hz, CH), 5.02 and 5.16 (m, $CH_2{=}$); ir (Nujol) 2540 (ν_{SH}), 1140 cm ($\nu_{C=S}$); *m/e* 175 (M^+), 142 ($M^+ - SH$); **3b,** mp 104–105°, which gradually decomposed on standing at room temperature; NMR ($CDCl_3$) δ 3.17 (d, *J* = 7.0 Hz, SH), 3.24 and 3.53 (s, $(CH_3)_2N-$), 5.54 (d, *J* = 7.0 Hz, CH), 7.30 ppm (m, C_6H_5); ir (Nujol) 2540 (ν_{SH}), 1140 cm ($\nu_{C=S}$); *m/e* 221 (M^+), 178 ($M^+ - SH$); **4a,** mp 66–67°; NMR ($CDCl_3$) δ 1.84 (s, $CH_3C{=}$), 2.07 (s, CH_3S), 3.38 and 3.49 (s, $(CH_3)_2N-$), 4.60 (s, CH), 5.00 and 5.08 ppm (m, $CH_2{=}$); ir (Nujol) 1140, 1112 cm ($\nu_{C=S}$); *m/e* 189 (M^+), 142 ($M^+ - SCH_3$); **4b,** mp 104–105°; NMR ($CDCl_3$) δ 2.08 (s, CH_3S), 3.21 and 4.46 (s, $(CH_3)_2N-$), 5.21 (s, CH), 7.20 −7.65 ppm (m, C_6H_5); ir (Nujol) 1140, 1112 cm ($\nu_{C=S}$); *m/e* 225 (M^+), 173 ($M^+ - SCH_3$).

The reaction conditions and yield are summarized in Tables I and II. A deep violet color, which develops upon metalation of **1** with organolithium reagent in HMPT–THF