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CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
TULANE UNIVERSITY, NEW ORLEANS, LOUISIANA 70118

β-Diketone Complexes of Cobalt(III). II. The Solvolysis Products of Sodium *trans*-Dinitrobis(acetylacetonato)cobaltate(III)[1]

BY BRILLE P. COTSORADIS AND RONALD D. ARCHER[2]

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The solvolysis stereochemistry of sodium *trans*-dinitrobis(acetylacetonato)cobaltate(III), $Na[Co(acac)_2(NO_2)_2]$ (acac = anion of acetylacetone), has been investigated in neutral and basic aqueous solutions as well as in dimethyl sulfoxide and methanol. The *trans*-dinitro ion rapidly hydrolyzes to the *trans*-nitroaquo complex. Equilibrium is established between the two species almost immediately, even below room temperature. The second hydrolysis step is several orders of magnitude slower. The visible spectrum of the base hydrolysis products indicates a mixture of products. Evidence for solvolyzed species also has been obtained in methanol and dimethyl sulfoxide. The *trans*-$[Co(acac)_2(NO_2)(H_2O)]$ and *cis*-$Na[Co(acac)_2(NO_2)_2]$ complexes have been prepared from *trans*-$Na[Co(acac)_2(NO_2)_2]$ using ion-exchange, freeze-drying, and solvent extraction procedures. A third complex, *cis*-$Na[Co(acac)_2(OH)_2]$, has been isolated in small yields from the base hydrolysis of sodium *trans*-dinitrobis(acetylacetonato)cobaltate(III). The configurations have been assigned to the complexes by correlation of pmr (pmr = proton magnetic resonance), infrared, visible, and ultraviolet spectra.

Introduction

A detailed study of bis(β-diketonato)cobalt(III) complexes[1b] has been initiated in this laboratory in order to determine the effect of ligand field strength on the reaction rates and product stereochemistry of cobalt(III) complexes. The absence of acidic protons on the donor atoms of the ligands makes the base hydrolysis reactions particularly interesting.

Sodium dinitrobis(acetylacetonato)cobalt(III) has recently been used by us[1b] and by other investigators[3] in the preparation of several new bis(acetylacetonato)cobalt(III) complexes. In order to elucidate the mechanisms which are important in reactions of this useful complex, a solvolysis study has been initiated. As a result of this investigation, several new complexes have been isolated and characterized.

Results and Discussion

Synthesis.—As noted below, the only previously reported[1b,3,4] isomer of $[Co(acac)_2(NO_2)_2]^-$ hydrolyzes rapidly in aqueous solution. Therefore, ion-exchange procedures have proven useful for the separation of the *trans*-nitroaquo ion of this series. Dissolution of the dinitro ion in cold water was followed by passage through a chloride-form ion-exchange column. The column exchanges chloride ions for unhydrolyzed $[Co(acac)_2(NO_2)_2]^-$, nitrite, and hydroxide ions. The exchange of nitrite ions prevents the reverse reaction of the equilibrium

$$trans\text{-}[Co(acac)_2(NO_2)_2]^- + H_2O \rightleftarrows trans\text{-}[Co(acac)_2(NO_2)(H_2O)] + NO_2^- \quad (1)$$

Concentration by freeze drying prevented further hydrolysis of the green solid, which was recrystallized from 95% ethanol and ether solutions.

The hydrated sodium *cis*-dihydroxobis(acetylacetonato)cobaltate(III) has been prepared from slightly basic solutions of *trans*-nitrobis(acetylacetonato)aquocobalt(III). The cold solutions were evaporated to dryness *in vacuo*. A green species was extracted from the resulting residues with chloroform and precipitated by the addition of ether. In aqueous solution, the green dihydroxo complex is adsorbed by anion ion-exchange resins. Since the anionic complex is soluble in chloroform as well as in water, ion-pair formation is apparent.

Sodium *cis*-dinitrobis(acetylacetonato)cobaltate(III) has been separated from the mixture of hydrolysis products which results when aqueous solutions of sodium *trans*-dinitrobis(acetylacetonato)cobaltate(III) are allowed to stand 1 week at room temperature. The *cis*-dinitro isomer was extracted with acetone and ethanol from the freeze-dried mixture of hydrolysis products of the *trans*-dinitro complex. The new isomer was recrystallized from acetone.

Proton Magnetic Resonance Spectra.—The proton magnetic resonance spectra of the *trans*-dinitro and the

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[1] (a) Extracted in part from the Ph.D. Dissertation of B. P. Cotsoradis, Tulane University, 1965; (b) part I of this series: R. D. Archer and B. P. Cotsoradis, *Inorg. Chem.*, **4**, 1584 (1965).

[2] Department of Chemistry, University of Massachusetts, Amherst, Mass. 01002.

[3] L. J. Boucher and J. C. Bailar, Jr., *J. Inorg. Nucl. Chem.*, **27**, 1093 (1965).

[4] A. Rosenheim and A. Garfunkel, *Ber.*, **44**, 1865 (1911). The isomer under discussion was originally prepared by these chemists. The *trans* configuration of the isomer was first postulated by Boucher and Bailar[3] on the basis of the infrared spectrum and chemical reaction product configurations.

trans-nitroaquo complexes have been measured at two temperatures in D_2O and CD_3OD. The pmr spectrum of the *trans*-dinitro complex in DMSO and the pmr spectrum of the *cis*-dinitro and the *cis*-dihydroxy complexes in D_2O also have been measured. The results are reported in Tables I and II.

TABLE I

PROTON MAGNETIC RESONANCE SPECTRA FOR SEVERAL BIS(ACETYLACETONATO)COBALT(III) COMPLEXES IN D_2O[a]

Complex	Position of CH_3[b] resonance peaks	Position of[b] CH resonance peaks
trans-[Co(acac)$_2$(NO$_2$)(H$_2$O)]	−2.28 (7)	−5.89 (1)
trans-Na[Co(acac)$_2$(NO$_2$)$_2$]	−2.18 (7)	−5.79 (1)
cis-Na[Co(acac)$_2$(NO$_2$)$_2$]	−2.10 (3)	−5.75 (1)
	−2.20 (3)	
cis-Na[Co(acac)$_2$(OH)$_2$][c]	−2.16 (3)	−5.82 (1)
	−2.22 (4)	

[a] Measurements were made on a Varian A-60 spectrometer using D_2O solutions of the complex. [b] Chemical shifts in ppm relative to the methyl peaks of sodium 3-trimethylsilyl-1-propanesulfonate (relative integrated intensities in parentheses). [c] The pmr peaks of this complex were broader than for the other complexes, possibly caused by traces of paramagnetic impurities.

TABLE II

PROTON MAGNETIC RESONANCE SPECTRA FOR TWO *trans*-BIS(ACETYLACETONATO)COBALT(III) COMPLEXES IN SEVERAL SOLVENTS[a]

Complex[b]	Solvent	Temp, °C	Position of CH_3 resonance peaks[c]	Position of CH resonance peaks[c]
[Co(acac)$_2$(NO$_2$)(H$_2$O)]	D_2O	4	−2.28 (6)[d]	−5.90 (1)[d]
[Co(acac)$_2$(NO$_2$)(H$_2$O)]	D_2O	23	−2.28 (7)[d]	−5.89 (1)[d]
[Co(acac)$_2$(NO$_2$)(H$_2$O)]	CD_3OD	4	−2.26 (6)[d]	−5.81 (1)[d]
[Co(acac)$_2$(NO$_2$)(H$_2$O)]	CD_3OD	23	−2.26 (8)[d]	−5.80 (1)[d]
Na[Co(acac)$_2$(NO$_2$)$_2$]	D_2O	4	−2.19 (2.1)[e]	−5.80
			−2.28 (1.0)[e]	−5.90
Na[Co(acac)$_2$(NO$_2$)$_2$]	D_2O	23	−2.18 (2.3)[e]	−5.79
			−2.28 (1.0)[e]	−5.90
Na[Co(acac)$_2$(NO$_2$)$_2$]	CD_3OD	4	−2.16 (1.3)[f]	−5.63
			−2.26 (1.0)[f]	−5.80
Na[Co(acac)$_2$(NO$_2$)$_2$]	CD_3OD	23	−2.15 (1.0)[f]	−5.61
			−2.25 (1.0)[f]	−5.79
Na[Co(acac)$_2$(NO$_2$)$_2$]	DMSO-d_6	23	−2.01 (4.5)[f]	−5.51
			−2.14 (1.0)[f]	−5.71
[Co(acac)$_2$(NO)$_2$(H$_2$O)][g] + NaNO$_2$	D_2O	23	−2.16 (6)[f]	−5.68
			−2.26 (1)[f]	*h*
Na[Co(acac)$_2$(NO$_2$)$_2$][i]	D_2O	4	−2.19 (1.52)[j]	*k*
			−2.28 (1.00)[j]	*k*
Na[Co(acac)$_2$(NO$_2$)$_2$][l] + NaNO$_2$	D_2O	4	−2.19 (3.81)[j]	*k*
			−2.28 (1.00)[j]	*k*

[a] Measurements were all made on a Varian A-60 spectrometer. [b] Except when indicated otherwise, solutions were saturated with the complex at 4°. The DMSO-d_6 (dimethyl sulfoxide) solution was saturated at room temperature. [c] Chemical shifts in ppm relative to tetramethylsilane in CD_3OD and DMSO-d_6 and relative to methyl groups of sodium 3-trimethylsilyl-1-propanesulfonate in D_2O; relative integrated intensities are in parentheses. In cases where two species are present, only the methyl peaks are integrated, since the intensities of CH peaks are only about one-sixth of the methyl peaks. [d] Peak integrated by spectrometer. [e] Peak intensities compared by multiplying height by width at half-height. [f] Peaks integrated by manual integration. [g] Prepared by mixing saturated solution of the complex with solutions of NaNO$_2$ at 23° in D_2O. [h] Peak unobserved. [i] A 0.0298 *M* solution. [j] Integrated by machine and by hand (by cutting out peaks and weighing paper). [k] Not measured. [l] A solution 0.0323 *M* in cobalt(III) plus 0.0249 *M* in added NaNO$_2$.

Whereas Boucher and Bailar[3] postulated the *trans* configuration for the long-known dinitrobis(acetylacetonato)cobaltate(III) isomer,[4] the pmr spectra of D_2O solutions of this species have two methyl peaks in a ratio of about 2:1 (both at 4 and 25°) as is possible for a mixture of *cis* and *trans* isomers—a situation observed in the case of *cis*- and *trans*-$[Co(acac)_2(NH_3)_2]^+$.[1b] Two CH peaks are also observed, which indicates that two species are in solution. However, the pmr spectrum of the nitroaquo species in D_2O corresponds to the low-field methyl and CH resonance peaks of the dinitro solutions. Similar results have been obtained in deuterated methanol, both at 4 and 25°. Therefore, the remaining methyl and CH peaks constitute the pmr spectrum of the dinitro complex. The presence of only a single, sharp methyl peak and a single CH resonance peak attributable to the dinitro complex and the isolation of the second isomer, as noted herein, confirms the previously hypothesized[3] *trans* configuration.

The single, sharp, methyl resonance peak and the single CH resonance observed in aqueous and methanolic solutions indicate that the nitroaquo complex has a *trans* configuration and that the solvolysis of the remaining nitro ligand is negligible under these conditions. However, the possibility of degenerate pmr peaks cannot be excluded, since it has been shown that the *cis*-bis(acetylacetonato)ethylenediaminecobalt(III) ion under similar conditions exhibits only a single methyl resonance, even though two are expected.[1b] Better instrumentation and solvent changes have resulted in the observation of a slight splitting in the latter case.[5]

The configurations of the *cis*-dinitro and the *cis*-dihydroxo complexes have been established by their pmr spectra. The *cis*-dinitro complex exhibits two equal CH_3 resonance peaks at −2.10 and −2.20 ppm and a single CH resonance peak at −5.75 ppm, and the

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(5) B. P. Cotsoradis and R. D. Archer, to be published.

cis-dihydroxo complex exhibits its CH_3 peaks at -2.16 and -2.22 ppm and a CH peak at -5.82 ppm. This type of spectrum is expected for a *cis*-bis(acetylacetonato) octahedral complex; *i.e.*, two equal CH_3 resonance peaks and a single CH resonance peak.[1b] Similar spectra had been previously obtained for bis(acetylacetonato)-2,2′-bipyridinecobalt(III) iodide, necessarily of a *cis*-type configuration, and *cis*-bis(acetylacetonato)-diamminecobalt(III) iodide.[1b]

Hydrolysis.—The high intensity of the pmr peaks of the nitroaquo complex immediately upon dissolution of the *trans*-dinitro complex in D_2O indicates a rapid solvolysis. A similar situation exists in both deuterated methanol and dimethyl sulfoxide. The intensity of the peaks due to the solvolyzed species is too great to be attributed to any impurity in the dinitro complex.[6]

The rapid attainment of equilibrium 1 between *trans*-$[Co(acac)_2(NO_2)(H_2O)]$ and *trans*-$[Co(acac)_2(NO_2)_2]^-$ in water has been shown conclusively by comparing the pmr spectrum of the nitroaquo species in D_2O, which has only a single methyl resonance peak, with a similar solution to which sodium nitrite in D_2O has been added (Table II). For the latter solution, the pmr peaks of the dinitro species immediately appear in the spectrum and a color change in the solution is visible. Thus, the attainment of equilibrium has been observed from both directions.

The equilibrium constant for eq 1 has been calculated on the basis of the integrated intensities of the methyl peaks of the two complex ions which result upon dissolution of the dinitro complex in deuterium oxide at 4°. A 0.0298 *M* solution indicated a 0.396:0.603 nitroaquo to dinitro ratio, whereas a solution 0.0323 *M* in total complex ion concentrations with 0.0249 *M* added nitrite (as $NaNO_2$) had a corresponding ratio of 0.208:0.792 for the nitroaquo and dinitro species. These solutions allow the calculation of *K* values of 7.75×10^{-3} and 8.30×10^{-3} *M*, respectively, where

$$K = \frac{[Co(acac)_2(NO_2)(D_2O)][NO_2^-]}{[Co(acac)_2(NO_2)_2^-]}$$

These solutions have pH values of 7 or higher. Under such conditions the hydrolysis of the nitrite ion does not significantly change the concentration of free nitrite ion. Therefore, the equilibrium constant for eq 1 at 4° in D_2O is 8×10^{-3} *M*.

The further hydrolysis of the *trans*-dinitro complex has been studied using pmr spectra. The pmr spectrum of a solution of the *trans*-dinitro and the *trans*-nitroaquo complexes in D_2O at room temperature gradually shows additional peaks. The new peaks were first observed after the complexes had been in solution about 8 hr. On each successive day, the relative intensities of the new peaks, which correspond to the peaks for the *cis*-dinitro complex, increased as the peaks attributed to the *trans*-dinitro and *trans*-nitroaquo species decreased. When aqueous solutions of the dinitro complex which had stood several days were extracted with chloroform, tris(acetylacetonato)cobalt(III) was isolated. This green complex was identified by pmr and infrared spectra. On the other hand, the pmr spectra of the solutions prior to extraction did not exhibit peaks which could be attributed to $[Co(acac)_3]$. This observation could be due to the low solubility of the tris complex in aqueous solutions saturated with ionic species. Because of the presence of the tris(acetylacetonato) species, it is impossible to say with certainty whether the *cis*-dinitro complex is formed directly from one of the two *trans*-bis(acetylacetonato)cobalt(III) species, or whether the acetylacetonato ligands exchange during the isomerization.

Octahedral *trans* Effect.—The *trans* effect of the nitro ligand in cobalt(III) complexes[3,7] appears to be operative in these complexes. In the present study we have observed considerable rapid aquation of the *trans*-dinitrobis(acetylacetonato)cobaltate(III) ion. On the other hand, the corresponding *cis* ion does not appear to aquate appreciably, even after standing several hours. Whether this is a kinetic or a thermodynamic effect has not been fully ascertained. Isotopic exchange studies should clarify this point.

Whereas the *trans* effect of the sulfito ligand appears to be quite general,[8] the nitro group gives a specific *trans* effect. That is, we have observed the attainment of equilibrium almost instantaneously by both water and nitro ligands *trans* to a nitro ligand, whereas Boucher and Bailar[3] noted no amine exchange for the same system. The latter investigators had also noted the rapid reactivity of one nitro ligand of the *trans*-dinitro species, but could draw no definite conclusions since the *cis* isomer was unknown at the time.

Infrared Spectra.—The infrared spectra of the new complexes (Table III) appear quite normal.[1b,3,9] and comparison with other spectra helped to identify the new species before elemental analyses had been obtained. Of particular interest are the bands attributable to the nitro group in the *cis*-dinitro complex.

In addition to the absorptions observed for the anhydrous *trans*-dinitro complex,[1b,3] a peak at 1340 cm^{-1} and a shoulder (840 cm^{-1}) on the lower frequency nitro band are indicative of the lower symmetry of the *cis* isomer. An increase in the multiplicity of some infrared peaks previously had been observed for *cis* isomers of cobalt(III) complexes.[10]

Visible and Ultraviolet Spectra.—The absorption maxima of the *cis*- and *trans*-dinitro, the nitroaquo,

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[6] The elemental analysis for the dinitro ion (*cf.* the Experimental Section) indicates that the carbon, hydrogen, and nitrogen contents are within experimental error of the calculated values. Although the analyses would still be within experimental error if the compound contained as much as 3 or 4% $[Co(acac)_2(NO_2)(H_2O)]$, the observation of 17–50% of solvolyzed complex immediately after dissolution cannot be due to trace impurities.

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TABLE III

CHARACTERISTIC INFRARED PEAKS OF SEVERAL BIS(ACETYLACETONATO)COBALT(III) COMPLEXES[a]

cis-Na[Co(acac)$_2$-(NO$_2$)$_2$]	*trans*-[Co(acac)$_2$-(NO$_2$)(H$_2$O)]	*cis*-Na[Co(acac)$_2$-(OH)$_2$]	Assignment
		1630 s	HOH bend
1567 s	1555 s	1560 s	$\mathrm{C}\overset{\cdots}{-}\mathrm{C}$ str[b]
1517 s	1514 s	1510 s	$\mathrm{C}\overset{\cdots}{-}\mathrm{O}$ str[b]
1413 s	1440 s	1420 sh	acac combination[b]
1370 s	1368 s	1378 s	CH$_3$ def
1340 ms			NO$_2$ str
1315 s	1315 s		NO$_2$ str
1280 m	1280 m	1265 s	acac combination[b]
1026 m	1028 m	1028 m	CH$_3$ rock
937 m	940 m	936 m	acac combination[b]
840 sh			NO$_2$ bend
832 m	820 m		NO$_2$ bend
		828 w	MOH bend
	800 w		
780 w	776 m	758 m	Ring H (acac), out-of-plane bend

[a] Spectral intensities: s, strong; m, medium; w, weak; sh, shoulder. Readings in cm^{-1}. [b] See ref 9.

and the dihydroxo cobalt(III) complexes are reported in Table IV. The assignments have been made on the basis of previous interpretations.[1b,3,11] The $^1A_{1g} \rightarrow {}^1T_{1g}$ assignment for the visible peak has been made on the basis of O$_h$ microsymmetry rather than the actual symmetry of each complex ion, since no splitting of this peak has been observed.[12] The reported value of 18,800 cm^{-1} (532 mμ)[3] for the maximum of the $^1A_{1g} \rightarrow {}^1T_{1g}$ transition for the *trans*-dinitro complex was in error because of the solvolysis of the complex. The maximum expected from the spectrochemical series for cobalt(III)[13] would be higher in energy. The positions for the corresponding transitions in the nitroammine,[3] the nitroaquo, and the dihydroxo complexes are at 18,700, 18,200, and 16,700 cm^{-1}, respectively—as might be expected on the basis of the spectrochemical series. Since our proton magnetic resonance studies have shown that aqueous solutions of the *trans*-dinitro complex contain measurable amounts of both the nitroaquo and the dinitro species, we have been able to calculate that the transition of the *trans*-dinitro complex occurs at about 19,300 cm^{-1} with a molar extinction coefficient of about 180, almost identical with the results for the *cis* complex.

TABLE IV

VISIBLE AND ULTRAVIOLET SPECTRA OF SEVERAL BIS(ACETYLACETONATO)COBALT(III) COMPLEXES[a]

	trans-[Co(acac)$_2$(NO$_2$)(H$_2$O)]	*cis*-Na[Co(acac)$_2$(OH)$_2$][b]	*cis*-Na[Co(acac)$_2$(NO$_2$)$_2$]	*trans*-Na[Co(acac)$_2$(NO$_2$)$_2$][c]
$^1A_{1g} \rightarrow {}^1T_{1g}$	18,200 (2.06)	16,700 (2.10)	19,200 (2.25)	19,300 (2.24)[d]
$t_{2g} \rightarrow \pi^*$(acac)	30,000 (3.78)	31,100 (3.71)	31,200 (3.98)[d]	
$\pi \rightarrow \pi^*$(acac)	40,800 (4.36)[d]	39,400 (4.28)[d]	39,400 (4.55)	
$\pi \rightarrow \pi^*$(acac)	43,900 (4.40)	43,500 (4.37)	43,700 (4.44)[d]	

[a] All peaks are given in cm^{-1} with log ϵ values given in parentheses. Samples were dissolved in water and spectra were taken at 0°. [b] Values were calculated from a single measurement. [c] Value determined from solution containing both *trans*-dinitro and *trans*-nitroaquo complexes. [d] Shoulder, values only approximate.

Base Hydrolysis.—Whereas the first step of the hydrolysis of the dinitro complex is very rapid, even in neutral solution, the second hydrolysis step competes with released nitrite ion only in basic solution. Furthermore, it is apparent that the second hydrolysis step involves a change in configuration, since the green *cis*-dihydroxo isomer has been isolated from basic solutions of the hydrolysis reaction products.

Spectral studies at 0° (Figure 1) show that the isolated *cis*-dihydroxo species is a secondary product of the reaction of the hydroxonitro species with hydroxide ion. The spectrum of the *trans*-hydroxonitro species was obtained by the addition of base to the corresponding nitroaquo complex and extrapolation of the successive spectra back to zero time. Although the *trans*-hydroxonitro and *cis*-dihydroxo species have an isosbestic point at about 502 mμ (ϵ 64), the absorbance at this wavelength during the base hydrolysis decreases by about 10% during the first 1000 sec and then climbs back to the starting point after 2500 sec and slowly continues upward. These changes, plus observations with the *trans*-dinitro species in basic solution, imply an intermediate species which has not been isolated. The ensuing increase in absorbance beyond the value of the isolated *cis*-dihydroxo species conceivably could be due to olation. In fact, highly absorbing brown species have been observed in the synthetic reactions. Further work to elucidate the hydrolysis mechanism is in progress.

Experimental Section

Acetylacetone.—Acetylacetone was obtained commercially and used without further purification.

Sodium *trans*-Dinitrobis(acetylacetonato)cobaltate(III).—The complex was prepared and purified as previously described.[1b]

Anal. Calcd for $C_{10}H_{14}O_8N_2CoNa$: C, 32.27; H, 3.76; N, 7.53. Found:[14] C, 32.41; H, 3.92; N, 7.42.

***trans*-Nitrobis(acetylacetonato)aquocobalt(III).**—Six grams (16.2 mmoles) of sodium *trans*-dinitrobis(acetylacetonato)cobaltate(III),[1b,3,4] which had been washed thoroughly with two 25-ml portions of acetone, was dissolved in about 200 ml of CO$_2$-free ice water. The resulting solution was passed through a 2-in. jacketed ion-exchange column, which was filled to a height of 12 in. with Dowex 1-X8 chloride ion exchange resin, 50–100 mesh. The column was maintained at 0°, by circulating ice water through the jacket. The neutral and cationic species were eluted from the column with CO$_2$-free ice water. The eluent which was green (approximately 400 ml) was frozen and freeze dried to a volume of about 40 ml. The dark green crystals which

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[11] D. W. Barnum, *J. Inorg. Nucl. Chem.*, **21**, 221 (1961); D. W. Barnum, *ibid.*, **22**, 183 (1961).

[12] B. P. Cotsoradis, Ph.D. Dissertation, Tulane University, 1965.

[13] F. Basolo, C. J. Ballhausen, and J. Bjerrum, *Acta Chem. Scand.*, **9**, 810 (1955).

[14] Elemental analyses by Huffman Laboratories, Inc., Wheatridge, Colo., Galbraith Laboratories, Inc., Knoxville, Tenn.; Alfred Bernhardt Mikroanalytisches Laboratorium, Ruhr, West Germany.

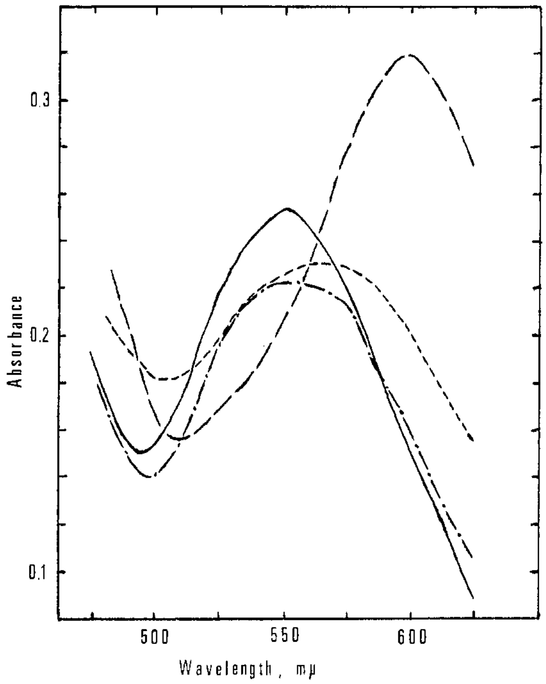

Figure 1.—The absorption spectra of 2.56 × 10^{-3} *M* aqueous solutions of *trans*-$[Co(acac)_2(NO_2)(OH)]^-$, ———, of *cis*-$[Co(acac)_2(OH)_2]^-$, — — —, and of *trans*-$[Co(acac)_2(NO_2)(OH)]^-$ also 3.69 × 10^{-3} *M* in NaOH after 1000 sec, — · —, and after 4000 sec, - - - -. The nitrohydroxo spectrum is based on the spectrum of the nitroaquo complex in basic solution before base hydrolysis occurs.

remained when the frozen mixture was allowed to melt were filtered from the solution and washed with ice water, ethanol, chloroform, and ether; yield of crude product, 1.1 g, 21%.

The crude green crystals of $[Co(acac)_2(NO_2)(H_2O)]$ were recrystallized by distillation in approximately 40 ml of 95% ethanol at room temperature. The resulting solution was filtered and evaporated to one-fourth of its volume using a rotary evaporator. Ether (5–10 ml) was added. The mixture was cooled and filtered. The crystals were washed with two 5-ml portions of ether; yield of recrystallized product, 0.75 g, 14%. *Anal.* Calcd for $C_{10}H_{16}O_7NCo$: C, 37.39; H, 4.99; N, 4.36. Found: C, 37.33; H, 5.10; N, 4.69.

Sodium *cis*-Dihydroxobis(acetylacetonato)cobaltate(III).—Starting as above, solutions of *trans*-nitrobis(acetylacetonato)-aquocobalt(III) eluted from the column were diluted to 2 or 3 times their initial volume with ice water. Sodium hydroxide (1 *M*) was added dropwise to the cold solutions until the pH was about 8.5 (as determined by Hydrion pH paper with an 8–10 pH range). The cold solutions were stirred several hours while the pH was maintained at 8.5. When the solutions turned emerald green, they were frozen.

The resulting green solutions were concentrated to about one-fifth to one-tenth their original volume by crushing the frozen solutions in a plastic bag and allowing the ice to melt partially. The resulting solutions were removed by filtration, and the remaining ice was discarded. The concentrated green solutions were evaporated to dryness by vacuum distillation. The temperature of the solutions was kept close to 0° at all times. The residue was further dried in a vacuum desiccator over KOH for several hours.

The dried residue was treated 3 times with 15 ml of $CHCl_3$ and then filtered after each extraction with $CHCl_3$. The $CHCl_3$ solution was green and the remaining residue was brown. About 100 ml of ether was added to the green $CHCl_3$ solution. Fine green crystals precipitated. The solution was allowed to cool and was filtered by suction. The green precipitate was washed with ether; yield, 0.13 g, 2%. *Anal.* Calcd for $C_{10}H_{16}O_6CoNa\cdot{}^3/_2H_2O$: C, 35.20; H, 5.42; N, 0.00. Found: C, 34.99; H, 5.02; N, 0.29.

Sodium *cis*-Dinitrobis(acetylacetonato)cobaltate(III).—Sodium *trans*-dinitrobis(acetylacetonato)cobaltate(III) (6.0 g, 16.2 mmoles) was dissolved in about 100 ml of water at room temperature in a 125-ml erlenmeyer flask. The solution, including any undissolved complex, was allowed to stand at room temperature for about 6 days and then was filtered. About 1.3 g of side products, which appeared to be $Co(acac)_3$ and $Co(acac)_2\cdot 2H_2O$, was removed from the solution by filtration.

The filtrate was extracted first with 50 ml of chloroform, twice with 25 ml of chloroform, and finally with 10 ml of chloroform. The chloroform removed more green side product, $[Co(acac)_3]$. The remaining aqueous solution was quickly frozen, and the mixture was freeze dried.

The freeze-dried product (4.1 g) was extracted with 25 ml of chloroform, 25 ml of a solution of acetone and ethanol (4:1 by volume), and 25 ml of acetone successively. The ethanol–acetone and acetone fractions were combined, and 100 ml of ether was added to the solution. A fine red precipitate formed immediately. The solution was cooled in an ice bath and then was filtered. The precipitate was washed twice with 5-ml portions of ether; yield of crude product, 1.5 g, 25%.

The crude product was recrystallized twice. First it was recrystallized by dissolution in 150 ml of acetone, filtration, and precipitation of the product with 100 ml of ether. The once-recrystallized product (0.8 g) was dissolved in 55 ml of a solution of acetone and ethanol (4:1 by volume) and then filtered. Ether (50 ml) was added to the filtrate. The solution was allowed to cool and then was filtered. The precipitate was washed twice with 5-ml portions of ether; yield of recrystallized product, 0.55 g, 9%. *Anal.* Calcd for $C_{10}H_{14}O_{10}N_3CoNa_2$: C, 27.21; H, 3.18; N, 9.53. Found: C, 27.15; H, 3.17; N, 9.28.

The analysis indicates that the product precipitates as a double salt, *cis*-$Na[Co(acac)_2(NO_2)_2]\cdot NaNO_2$. In order to obtain the desired complex, the double salt was recrystallized from acetone. As acetone was added to the complex, the mixture was stirred until about half of the salt dissolved, and then the solution was filtered. An equal volume of ether was added to the solution, and the solution was allowed to cool. The solution was filtered and the red precipitate was washed with ether. *Anal.* Calcd for $C_{10}H_{14}O_8N_2CoNa$: C, 32.27; H, 3.76; N, 7.53. Found: C, 32.30; H, 3.80; N, 7.36.

Determination of the Equilibrium Constant.—The equilibrium constant *K*, where

$$K = \frac{[Co(acac)_2(NO_2)(D_2O)][NO_2^-]}{[Co(acac)_2(NO_2)_2^-]}$$

was determined by dissolving weighed samples of pure *trans*-$Na[Co(acac)_2(NO_2)_2]$ in D_2O in volumetric flasks at 4°. After 1 hr, the pmr spectra were taken on a Varian Model A-60 equipped with temperature control. The concentrations of the two complex species were determined from the integrated intensities of their pmr peaks. Both machine integration and hand integration (cutting out peaks and weighing) were used. The $[NO_2^-]$ was the sum of the concentration of $[Co(acac)_2(NO_2)(D_2O)]$ and the concentration of the NO_2^- originally added to the solution. These values were substituted into the equilibrium expression.

Determination of the Extinction Coefficients of Sodium *trans*-Dinitrobis(acetylacetonato)cobaltate(III).—The visible spectra were obtained for the same solutions used to determine *K*. A path length of 0.10 cm was used in measuring the spectra. The extinction coefficients for the *trans*-dinitrobis(acetylacetonato)-cobalt(III) complex could be calculated since the concentrations of both species were known from the pmr spectra and the extinction coefficients of *trans*-$[Co(acac)_2(NO_2)(H_2O)]$ had been previously determined.

Infrared Spectra.—All infrared spectra were obtained on a Beckman Model IR-5A infrared spectrophotometer. Potassium bromide pellets of the complexes were prepared and used for obtaining the spectra.

Visible–Ultraviolet Spectra.—The visible and ultraviolet spectra of all the complexes were obtained with a Cary Model 14 recording spectrophotometer using aqueous solutions in 1-cm cells or, in one case, using 1-cm cells with 0.9-cm cell spacers which gave 0.1-cm path lengths.

Proton Magnetic Resonance.—All pmr spectra were obtained on a Varian Model A-60 high-resolution spectrometer, using tetramethylsilane as an internal standard in CD_3OD and C_2D_6SO, and using the methyl peaks of sodium 3-trimethylsilyl-1-propanesulfonate as a reference in D_2O. The Varian temperature control unit of the spectrometer was calibrated from the temperature dependence of the methanol resonance peaks, as recommended by the manufacturer.

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CONTRIBUTION FROM THE DIVISION OF MINERAL CHEMISTRY,
CSIRO, MELBOURNE, AUSTRALIA

Heat of Formation and Bond Energy of Bis(cyclopentadienyl)magnesium

By H. S. HULL, A. F. REID, and A. G. TURNBULL

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The standard heat of formation of $Mg(C_5H_5)_2(c)$ at 298°K is measured to be 16.0 ± 0.8 kcal/mole from the heat of hydrolysis in 1 N H_2SO_4. Mass spectrometric appearance potentials are used to derive the standard heat of formation of $C_5H_5(g)$, 53 ± 12 kcal/mole. From these data and the heats of sublimation of $Mg(C_5H_5)_2$, 16.3 ± 0.3 kcal/mole, and Mg, 35.3 ± 0.3 kcal/mole, the mean magnesium–radical bond energy is found to be 54.5 ± 12 kcal/mole. Reevaluation of literature data gives mean bond energies of 53 and 77 kcal/mole for $Ni(C_5H_5)_2$ and $Fe(C_5H_5)_2$, respectively.

Introduction

Metal–cyclopentadienyl compounds exhibit a wide range of chemical behavior and a variation of bond type between ionic and π-covalent extremes. The chemical stability may be quantitatively defined by the free energy change, ΔG_r, of appropriate reactions, while the bond type may be characterized by the mean metal–radical bond energy, $\bar{B}$.

Values of free energy of formation, $\Delta G_f{}^\circ$, and bond energy, $\bar{B}$, are available only for the π-bonded compounds $Fe(C_5H_5)_2$ and $Ni(C_5H_5)_2$, for which heats of combustion[1] and vaporization[2] have been combined with both measured and calculated[3,4] entropies. In the present work $\Delta G_f{}^\circ$ and $\bar{B}$ are derived for $Mg(C_5H_5)_2$ from the heat of hydrolysis in 1 N H_2SO_4. This method avoids difficulties with incomplete combustion and formation of energy-rich oxides and should be applicable to many cyclopentadienyl–metal compounds which hydrolyze readily. It is found that $Mg(C_5H_5)_2$ is more stable with respect to the elements than $Fe(C_5H_5)_2$ by 18 kcal/mole, even though the $Mg-C_5H_5$ bond is 22 kcal/mole weaker than the $Fe-C_5H_5$ bond.

Experimental Section

Bis(cyclopentadienyl)magnesium, $Mg(C_5H_5)_2$, was prepared, purified, and analyzed as previously described.[5] Samples were vacuum sublimed into thin Pyrex bulbs which were sealed off and weighed with vacuum corrections. The bulbs were broken under 120 g of nitrogen-flushed 1 N H_2SO_4 in a platinum calorimeter previously described.[6] The reaction was rapid and heat evolution complete within 1 min. The aqueous solution was analyzed for Mg for two runs by titration with EDTA which had been standardized against 99.99% Mg metal dissolved in 1 N H_2SO_4. The glass pieces were collected and weighed and sample weights obtained by difference. Based on these sample weights, the two analyses gave for Mg 15.6, 16.0 wt %; calcd 15.7 wt %. Separate analysis established that no magnesium remained in the organic phase.

Two electrical calibrations, agreeing within ±0.2%, were performed after each reaction. Operation of the calorimeter was satisfactorily checked by measuring the heat of solution of Mg metal in 1 N HCl.[6] A thin layer of freshly distilled liquid cyclopentadiene was placed on the surface of the sulfuric acid to ensure that cyclopentadiene formed by hydrolysis of $Mg(C_5H_5)_2$ was in the liquid state and to ensure saturation of the acid with cyclopentadiene. The calorimeter was closely, but not completely, sealed to avoid excessive evaporation. A small correction amounting to $0.16v$ cal was added to the observed heat evolution to allow for evaporation of C_5H_6 and H_2O into the evacuated volume v of the sample bulbs on breaking. The correction was calculated from the known vapor pressures and heat of vaporization of C_5H_6[5] and H_2O[7] at the calorimeter temperature. The volume v was the measured external bulb volume (2–3 cm^3), corrected for glass and sample volumes. Blank runs with empty bulbs confirmed the magnitude of this calculated correction.

The heat absorbed by vaporization of C_5H_6 and H_2O into the free space of the calorimeter (15 cm^3) due to a temperature rise ΔT was calculated to be $0.10\Delta T$ cal. This amounted to <0.1% of total heat for both reaction and calibration and hence cancelled out within experimental error.

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