Table V

Esr Parameters for $[LCoS_4C_4(CF_3)_4]^0$

L	$\langle g \rangle$ [a]	$\langle A \rangle$ for Co,[a] gauss	$g_{\|}$[b]	$A_{\|}$[b] for Co, gauss
$(C_6H_5O)_3P$	2.0165	26.4[c]	2.0160	62.95
$(C_6H_5)_3P$	2.0192	28.83	2.0193	74.99
$(C_6H_5)_3As$	2.0197	31.15	2.0248	80.74
$(C_6H_5)_3Sb$	2.0302	d	2.0497	81.28

[a] Obtained in chloroform solution. [b] Obtained from frozen toluene solution at ~100°K. Perpendicular components insufficiently resolved. [c] ^{31}P hyperfine splitting of 9.3 gauss. [d] Complex solution spectrum not yet interpreted.

havior has been noted with the nickel group dithiolate anions $[MS_4C_4(CN)_4]^-$. These species are monomeric, $S = {}^1/_2$ species in solution. However, in the solid state metal-to-sulfur interactions between planar anions results in antiferromagnetic behavior and a diamagnetic ground state.[21,22]

The monoanions $[(C_6H_5)_3PCoS_4C_4(CF_3)_4]^-$ and $[(C_6H_5)_3PCoS_4C_4(CN)_4]^-$ [6] are diamagnetic. The magnetic moment of $[(C_4H_9)_4N][(C_6H_5)_3PFeS_4C_4(CF_3)_4]$ indicates an $S = {}^3/_2$ ground state with very little orbital contribution. Several other five-coordinate iron complexes with quartet ground states are known; these include $[(R_2NCS_2)_2FeX]$ (R = alkyl; X = Cl, Br, I),[23] which are known to have square-pyramidal geometry,[24] and $[(C_4H_9)_4N][C_5H_5NFe(S_2C_6H_3CH_3)_2]$.[25]

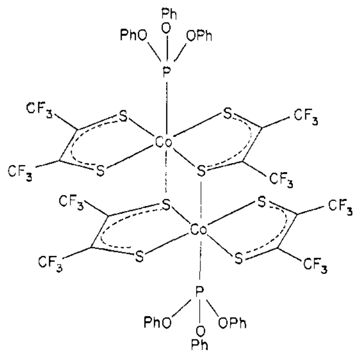

Figure 4.—Proposed structure for $(C_6H_5)_3PCoS_4C_4(CF_3)_4$ in the solid state.

Acknowledgment.—Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research. We thank Dr. F. Ann Walker for the esr measurements.

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[22] C. J. Fritchie, *Acta Cryst.*, **20**, 107 (1966).

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[25] R. Williams, E. Billig, J. H. Waters, and H. B. Gray, *J. Am. Chem. Soc.*, **88**, 43 (1966).

Contribution from the Department of Chemistry,
Carnegie Institute of Technology, Pittsburgh, Pennsylvania 15213

Stereochemistry of β-Diketone Complexes of Cobalt(III). II. Preparation and Properties of Coordination Compounds with Two Unsymmetrical 1,3-Diketone Ligands[1]

By L. J. BOUCHER

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Cobalt(III) complexes of two unsymmetrical β-diketones, 1-methoxy-2,4-pentanedione and 2,4-hexanedione, have been studied. Coordination compounds of the types sodium dinitrobis(β-diketonato)cobaltate(III), nitropyridinebis(β-diketonato)cobalt(III), and ethylenediaminebis(β-diketonato)cobalt(III) iodide have been synthesized. The ultraviolet, visible, infrared, and nuclear magnetic resonance spectral properties of the complexes have been measured. The configuration of the third series of complexes is necessarily *cis* while that of the first two series is assumed to be the same as that of an analogous acetylacetone complex, *i.e.*, *trans*. Chemical and spectral evidence is consistent with this assignment. Both the *cis* and *trans* complexes can exist as additional geometrical isomers (with respect to the unsymmetrically substituted β-diketones). Proton magnetic resonance spectra suggest that the materials isolated are mixtures of all of the possible isomers.

Although substitution, isomerization, and racemization reactions of transition metal complexes have been extensively studied,[2] surprisingly little is known about the reactions of transition metal complexes of weak field bidentate ligands. Archer has suggested that complexes of β-diketones might show reaction pathways substantially different from those already observed.[3] These anionic ligands form coordination compounds of reduced positive charge that contain no acidic protons, and nuclear magnetic resonance (nmr) spectroscopy can be used in studying stereochemical changes in the reactions of their complexes.[4] The isomerization and racemization reactions of some tris(β-diketonato)cobalt-

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

[2] F. Basolo and R. G. Pearson, "Mechanism of Inorganic Reactions," 2nd ed, John Wiley and Sons, Inc., New York, N. Y., 1967.

[3] R. D. Archer in "Werner Centennial," Advances in Chemistry, No. 62, American Chemical Society, Washington, D. C., 1967, p 452.

[4] R. C. Fay and T. S. Piper, *Inorg. Chem.*, **3**, 348 (1964).

(III) complexes have been thoroughly investigated.[4–6]

The solvolysis reaction of *cis* and *trans* cobalt(III) complexes with two acetylacetone ligands has been studied by Cotsoradis and Archer.[7] Similar octahedral complexes containing two unsymmetrical β-diketone chelates can exist as a number of geometrical isomers, with respect to the unsymmetrically substituted ligands. The use of these stereochemical labels should allow a decision to be made about the relative importance of different reaction pathways. Sodium *trans*-dinitrobis(acetylacetonato)cobaltate(III) was first prepared by Rosenheim and Garfunkel.[8] In part I of this series the syntheses of the *trans*-nitroaminebis(acetylacetonato)cobalt(III) complexes were reported. Archer and Cotsoradis recently published the preparation of some *cis*- and *trans*-diamine- and *cis*-dinitrobis(acetylacetonato)cobaltate(III) salts.[7,9] A previous attempt was made to synthesize analogous complexes except that unsymmetrical β-diketones were used.[10] This paper reports the results of a continuation of that work.

Experimental Section

Preparation of Complexes.—All ligands and sodium cobaltinitrite were obtained commercially and used without further purification.

$Na[Co(dik)_2(NO_2)_2]$.[11]—A solution of 15 g (0.037 mole) of sodium cobaltinitrite in 50 ml of water was mixed with 50 ml of a solution of 3.2 g (0.08 mole) of sodium hydroxide and 10.4 g (0.08 mole) of methoxyacetylacetone or 9.1 g (0.08 mole) of propionylacetone. The resulting solution was stirred for a few minutes and then allowed to stand for 48 hr at room temperature. The mixture was filtered; the red solid was collected and washed with acetone (until the washings were colorless) and air dried. The crude product was rapidly dissolved in 100 ml of water and the mixture filtered into 100 ml of a saturated solution of sodium nitrite, whereupon the pure solid precipitated. $[Co(macac)_2(H_2O)_2]$ appears to be more soluble in water than $Na[Co(macac)_2(NO_2)_2]$. Dissolution of the initial precipitate is best carried out with 50 ml of water (discarded) and then with 400 ml of water. The second fraction was filtered into 100 ml of saturated sodium nitrite solution. The orange-red powder was collected on a filter, washed with a little cold water. acetone, and ether, and air dried; yield 1.6 g, ~10%.

Anal. Calcd for $Na[Co(macac)_2(NO_2)_2]\cdot H_2O$, $C_{12}H_{18}N_2O_{10}CoNa\cdot H_2O$: C, 32.00; H, 4.49; N, 6.22. Found: C, 32.41; H, 4.34; N, 6.09.[12]

Anal. Calcd for $Na[Co(prac)_2(NO_2)_2]\cdot H_2O$, $C_{12}H_{18}N_2O_8CoNa\cdot H_2O$: C, 34.45; H, 4.83; N, 6.69. Found: C, 34.02; H, 4.79; N, 6.16.

$[Co(dik)_2NO_2py]$.—To a mixture of 2.1 g (0.005 mole) of $Na[Co(prac)_2(NO_2)_2]\cdot H_2O$ or 2.2 g (0.005 mole) of $Na[Co(macac)_2(NO_2)_2]\cdot H_2O$ and 50 ml of water, 7.9 g (0.1 mole) of pyridine was added and the resulting mixture was stirred at room temperature for 15 min. The red solid was collected on a filter and washed twice with 50 ml of water and air dried. The crude product was recrystallized from boiling absolute ethanol, washed wih ether, and air dried; yield ~0.8 g, ~40%.

Anal. Calcd for $[Co(prac)_2NO_2py]$, $C_{17}H_{23}N_2O_6Co$: C, 49.76; H, 5.68; N, 6.82. Found: C, 49.67; H, 5.83; N, 6.67; mp, 156°.

Anal. Calcd for $[Co(macac)_2NO_2py]$, $C_{17}H_{23}N_2O_8Co$: C, 46.15; H, 5.25; N, 6.33. Found: C, 45.80; H, 5.30; N, 6.20; mp, 136°.

$[Co(dik)_2en]I$.—A solution of 1.5 g (0.025 mole) of ethylenediamine in 50 ml of water was added dropwise to a mixture of 10.4 g (0.025 mole) of $Na[Co(prac)_2(NO_2)_2]\cdot H_2O$ or 11.3 g (0.025 mole) of $Na[Co(macac)_2(NO_2)_2]\cdot H_2O$ and 2.0 g of Norit A neutral activated charcoal in 200 ml of water. The resulting mixture was stirred at room temperature for 15 min and filtered, and the charcoal was washed with 25 ml of water. The combined filtrate was then evaporated to dryness in an air stream. The residue was extracted with acetone, and then the purple solution was evaporated to dryness on a rotatory evaporator. The residue was dissolved in 10 ml of water and filtered, and 10 g of potassium iodide was added. Purple-red crystals separated and were collected on a filter, washed with a little cold water and ether, and air dried; yield ~3.0 g, ~25%.

Anal. Calcd for $[Co(macac)_2en]I$, $C_{14}H_{26}N_2O_6CoI$: C, 33.35; H, 5.20; N, 5.56. Found: C, 33.51; H, 5.24; N, 5.44.

Anal. Calcd for $[Co(prac)_2en]I$, $C_{14}H_{25}N_2O_4CoI$: C, 35.55; H, 5.54; N, 5.92. Found: C, 35.41; H, 5.36; N, 5.97.

Spectral Meacurements.—Infrared spectra were obtained with a Perkin-Elmer Model 21 spectrophotometer in the 4000–650-cm^{-1} region. The complexes were in potassium bromide disks and also in Nujol mulls. The frequencies of the absorptions were reproduced to better than ± 4 cm^{-1}. Ultraviolet and visible spectra were measured with a Cary Model 11 recording spectrophotometer in the 210–700-mμ region. The broad absorption maxima could be estimated to ±2 mμ and the extinction coefficients were determined in each case using several solutions of different concentrations; maxima were found to conform to Beer's law. The materials were dissolved in distilled water (cationic complexes) or absolute ethanol (neutral complexes) and placed in 10-mm quartz cells. Nuclear magnetic resonance spectra were obtained at 38–40° with a Varian Associates Model A-60 high-resolution spectrometer. The materials were dissolved in $CDCl_3$, 10% (w/v) (neutral complexes), or D_2O, 5% (w/v) (cationic complexes). In the first case tetramethylsilane, 1–2% (v/v), was used as an internal standard and in the second case sodium 3-trimethylsilyl-1-propanesulfonate, 2% (w/v), was used. Chemical shifts were reproduced to at least ±0.02 ppm.

Results and Discussion

Syntheses.—The dinitrobis(β-diketonato)cobaltate(III) salts, with unsymmetrical β-diketones, can be prepared in the same way as the acetylacetone complex

$$[Co(NO_2)_6]^{3-} + 2(dik)^- \longrightarrow [Co(dik)_2(NO_2)_2]^- + 4NO_2^- \quad (1)$$

In addition to this material (~15%), a small portion of $[Co(dik)_3]$ and a much larger portion of $[Co(dik)_2]$ (~30%) are isolated for acetylacetone, propionylacetone, and methoxyacetylacetone. When trifluoroacetylacetone or benzoylacetone are used, the only product isolated other than a small amount of $[Co(dik)_3]$ is hydrated $[Co(dik)_2]$. A redox reaction involving the cobalt(III) ion can take place at any one of a number of stages. The reduction of $[Co(dik)_3]$, formed from a side reaction, seems unlikely due to the well-known stability of this species.[13] Similarly $[Co(dik)_2(NO_2)_2]^-$ does not readily yield $[Co(dik)_2]$ in neutral aqueous

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[5] R. C. Fay and T. S. Piper, *J. Am. Chem. Soc.*, **84**, 2303 (1962); **85**, 500 (1963).

[6] R. A. Palmer, R. C. Fay, and T. S. Piper, *Inorg. Chem.*, **3**, 875 (1964).

[7] B. P. Cotsoradis and R. D. Archer, *ibid.*, **6**, 800 (1967).

[8] A. Rosenheim and A. Garfunkel, *Ber.*, **44**, 1865 (1911).

[9] R. D. Archer and B. P. Cotsoradis, *Inorg. Chem.*, **4**, 1584 (1965).

[10] L. J. Boucher, Ph.D. Thesis, University of Illinois, 1964.

[11] Abbreviations used include: dik = enolate anion of a β-diketone; acac = 2,4-pentanedione (acetylacetone); prac = 2,4-hexanedione (propionylacetone); macac = 1-methoxy-2,4-pentanedione (methoxyacetylacetone); py = pyridine; en = ethylenediamine.

[12] All elemental analyses by Galbraith Laboratories, Inc., Knoxville, Tenn.

[13] J. P. Collman, "Transition Metal Chemistry," Vol. 1, R. L. Carlin, Ed., Marcel Dekker, Inc., New York, N. Y., 1966, p 1.

Table I

Absorption Maxima from Electronic Spectra of Complexes[a]

Compound	$^1A_{1g} \rightarrow {}^1T_{1g}$	$t_{2g} \rightarrow \pi^*$	$\pi \rightarrow \pi^*$	$\pi \rightarrow \pi^*$
$[Co(acac)_2NO_2py]$	18.9[b] (2.16)[c]	29.7 (3.9)	38.6 (4.4)	43.7 (4.4)
$[Co(prac)_2NO_2py]$	18.9 (2.15)	29.7 (3.9)	38.6 (4.4)	43.1 (4.4)
$[Co(macac)_2NO_2py]$	18.9 (2.16)	29.8 (3.9)	38.8 (4.4)	42.2 (4.4)
$[Co(acac)_2en]I$	18.7 (2.21)	30.8 (3.8)	40.2[d] (4.4)	Obs
$[Co(prac)_2en]I$	18.7 (2.20)	30.8 (3.8)	40.5[d] (4.4)	Obs
$[Co(macac)_2en]I$	18.7 (2.16)	30.8 (3.8)	40.3[d] (4.4)	Obs

[a] Samples were dissolved in water (cationic complexes) or absolute ethanol (neutral complexes). [b] kK = kilokaiser = 1000 cm^{-1}. [c] Log ϵ_{max} value in parentheses. [d] Shoulder; obs, obscured by anion absorption.

solution, over long periods of time. Reaction 1 undoubtedly proceeds *via* a stepwise addition of the β-diketone ligands to the cobalt atom. If the mono-β-diketone complex rapidly engaged in electron transfer (more rapidly than the addition of a second β-diketone ligand), then the cobalt(II) salt would build up in preference to the desired complexes. In some cases the reverse situation would be true. The redox reaction might involve the coordinated or free β-diketone or nitrite ion as reducing agents. Slightly different electronic structures for the β-diketone cobalt(III) complexes might account for the relative ease of electron transfer for some of the complexes. For example, trifluoroacetylacetone and benzoylacetone give rise to a weaker ligand field than does acetylacetone.[5] The ligand field strength should be approximately the same for acetylacetone, propionylacetone, and methoxyacetylacetone.

The chemical properties of the $[Co(dik)_2(NO_2)_2]^-$ salts appear to be entirely similar. For example, when pyridine is added to an aqueous solution of the complex, only the monopyridine complex is formed. This reaction and others probably proceed *via* an aquo intermediate.[7]

$$[Co(dik)_2(NO_2)_2]^- + H_2O \rightleftharpoons [Co(dik)_2NO_2H_2O] + NO_2^- \quad (2)$$

$$[Co(dik)_2NO_2H_2O] + py \longrightarrow [Co(dik)_2NO_2py] + H_2O \quad (3)$$

In the presence of charcoal, the reaction of $[Co(dik)_2(NO_2)_2]^-$ with ethylenediamine readily proceeds in aqueous solution

$$[Co(dik)_2(NO_2)_2]^- + en \xrightarrow{C} [Co(dik)_2en]^+ + 2NO_2^- \quad (4)$$

There is no reason to believe that reactions 3 and 4 would not take place with other amines to give complexes similar to those of acetylacetone.[1,4] Both the $[Co(dik)_2en]^+$ salts and the $[Co(dik)_2pyNO_2]$ complexes are stable to dissociation in neutral aqueous and alcoholic solutions for days at room temperature. Further, the absorption spectra are also unchanged when excess ligand of both types is added to the solution of the complexes.

Spectral Properties.—The electronic spectra of the complexes were recorded in the 700–210-mμ region. The absorption maxima and molar extinction coefficients are listed in Table I. Data for the corresponding acetylacetone complexes are given for comparison here, as well as in the other tables. Assignments are made by analogy to those for tris(acetylacetonato)cobalt(III).[14] Unfortunately, the $[Co(dik)_3]$ complexes for methoxyacetylacetone and propionylacetone have not been characterized.

Since no splitting of the broad ligand field band at 18.7–18.9 kK is noted, this absorption is assigned to the $^1A_{1g} \rightarrow {}^1T_{1g}$ transition (pseudo-O_h microsymmetry). The second ligand field band, $^1A_{1g} \rightarrow {}^1T_{2g}$, is not observed because it is obscured by the tail of the intense charge-transfer absorption in the ultraviolet region. The frequency of the visible maximum is independent of the β-diketone. On the other hand, it does show the expected red shift in going from the nitropyridine to the ethylenediamine complex. The spectra of the dinitro salts are not given here since these materials are expected to undergo rapid solvolysis in water to yield an equilibrium mixture of the dinitro and aquonitro complexes.[9] It is interesting to note that aqueous solutions of all of the $[Co(dik)_2(NO_2)_2]^-$ complexes have absorption maxima at 18.8 kK with log ϵ equal to 2.0. This may be indicative of an approximately equivalent extent of solvolysis for the three materials.

The ultraviolet spectra of the complexes show a charge-transfer absorption, $t_{2g} \rightarrow \pi^*$, and two higher energy $\pi \rightarrow \pi^*$ absorptions of the enolate anion. The metal–ligand charge-transfer band, at 29.7–30.9 kK, appears to be independent of the β-diketone. Conversely, it does show a substantial blue shift in going from the nitropyridine to the ethylenediamine complexes. The change may be a consequence of the different donor molecules present or may be linked to the change in stereochemistry; *i.e.*, the nitropyridine compounds are most likely *trans* while the ethylenediamine compounds are required to have the *cis* configuration. The latter explanation is supported by the observation that while *trans*-$[Co(acac)_2(NH_3)_2]^+$ shows the ligand field band at higher energy than the *cis* isomer, the reverse is true for the charge-transfer transition.[9] The lowest energy $\pi \rightarrow \pi^*$ enolate anion absorption, at 38.6–40.5 kK, is approximately independent of the β-diketone. This absorption does display the considerable blue shift in going from the nitropyridine to the ethylenediamine complexes. In contrast to the other bands, the high-energy $\pi \rightarrow \pi^*$ enolate anion absorption seems to be observably dependent on the β-diketone.[15]

Infrared spectra were recorded in the 4000–650-cm^{-1} region, with the complexes in potassium bromide disks.

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(14) D. W. Barnum, *J. Inorg. Nucl. Chem.*, **21**, 221 (1961); **22**, 183 (1961).

(15) A. E. Gillam and E. S. Stern, "Electronic Absorption Spectroscopy in Organic Chemistry," Edward Arnold, London, 1958.

TABLE II

INFRARED ABSORPTION MAXIMA FOR COMPLEXES[a]

$\mathrm{Na[Co(dik)_2(NO_2)_2]}$			$\mathrm{[Co(dik)_2NO_2py]}$			$\mathrm{[Co(dik)_2en]I}$			
acac	macac	prac	acac	macac	prac	acac	macac	prac	Assignment[19]
						3200 w	3190 w	3200 w	$\nu_{as}(\mathrm{NH_2})$
						3140 w	3140 w	3140 w	$\nu_s(\mathrm{NH_2})$
3060 w		3060 w	3060 w	3040 w	3060 w	3050 w	3070 w	3060 w	$\nu(=\mathrm{C}-\mathrm{H})$
2920 w	2920 w	2930 w	2970 w	2910 w	2920 w	2910 w	2910 w	2920 w	$\nu_{as}(\mathrm{CH_3})$
2900 w	2890 w	2890 w	2890 w	2870 w	2860 w				$\nu_s(\mathrm{CH_3})$
	2815 w			2800 w			2810 w		$\nu(-\mathrm{O}-\mathrm{CH_3})$
1550 s	1568 s	1563 s	1555 s	1572 s	1575 s	1572 s	1572 s	1570 s	$\nu(\mathrm{C}\overset{\cdots}{-}\mathrm{O})$
1520 s	1524 s	1520 s	1517 s	1517 s	1519 s	1517 s	1517 s	1520 s	$\nu(\mathrm{C}\overset{\cdots}{-}\mathrm{C})$
1449 m	1443 m	1443 m	1440 w	1440 w	1440 w				
1418 s	1425 s	1422 s	1420 s	1424 s	1430 s	1420 w	1445 w	1422 w	$\delta_{as}(\mathrm{CH_3})$
	1396 s	1402 s	1368 m	1394 s	1395 s	1379 s	1392 s	1391 s	$\delta_{as}(\mathrm{CH_3})$
1348 m	1355 m	1365 m	1340 m	1340 w	1342 s	1305 w	1358 w	1355 w	$\delta_s(\mathrm{CH_3})$
1308 m	1310 m	1309 m	1312 s	1319 s	1319 s				$\nu_s(\mathrm{NO_2})$
1286 m	1275 m	1285 m	1284 w	1278 w	1272 w	1277 m	1279 m	1277 w	$\nu(\mathrm{C}=\mathrm{C}) + \nu(\mathrm{C}-\mathrm{CH_3})$
1196 w	1200 m		1206 m	1207 w	1207 m				
	1182 w	1184 w	1186 w	1193 m	1182 m	1188 w	1195 m	1179 m	$\delta(=\mathrm{C}-\mathrm{H})$
				1152 w	1150 w	1129 m		1121 m	
	1110 s			1114 s			1112 s		$\nu_{as}(\mathrm{C}-\mathrm{O}-\mathrm{C})$
		1071 m			1070 w	1089 w		1072 w	
		1056 w	1066 m	1064 w	1061 m	1056 w	1053 w	1056 w	
1028 m	1025 w	1024 m	1024 m	1016 w	1027 w	1027 w	1024 w	1028 w	$\rho_r(\mathrm{CH_3})$
1016 w			1009 w		1015 w	1006 w	1005 w	1004 w	
	992 w	990 w		992 w	990 w	994 w	993 w	989 w	
948 m	958 w	960 m		962 w	960 w		963 w	957 w	
	932 w		939 m	942 w		933 m	924 w		
				921 w			920 w		
919 w									
		898 m			896 m			894 m	
824 s	825 s	824 s	818 s	818 s	818 s				$\pi(\mathrm{NO_2})$
797 m	797 w	814 w	785 m	792 w	800 w	799 m	790 m	802 m	$\pi(=\mathrm{C}-\mathrm{H})$
				777 m	782 m				$\pi(\mathrm{py}-\mathrm{H})$
		768 m			764 m			766 m	$\rho_r(-\mathrm{CH_2}-)$
	721 w		708 m	702 m	708 m				$\pi(\mathrm{py}-\mathrm{H})$
685 m	685 w	684 m	685 w	675 w	685 w	698 w		675 w	
662 w			664 w			660 m	650 m		

[a] In $\mathrm{cm^{-1}}$; w, weak; m, medium; s, strong.

The frequencies of the absorptions are listed in Table II. Assignments are based on previous studies of the infrared spectral properties of acetylacetone[16] or ethylenediamine[17] complexes as well as on group frequency correlations of organic compounds.[18]

While the electronic spectra often do not allow a clear distinction to be made among the complexes of the different β-diketones, the infrared spectra do. For example, only the methoxyacetylacetone complexes show strong absorption at 1100 $\mathrm{cm^{-1}}$ which can be assigned to the ether –C–O–C– antisymmetric stretch. Further, a weak absorption at 2810 $\mathrm{cm^{-1}}$ can be attributed to the C–H stretch of the ether group. Only the spectra of the propionylacetone complexes show bending and rocking absorptions (among others) of the ethyl group at 1070, 896, and 766 $\mathrm{cm^{-1}}$. Most of the other absorptions listed in Table II arise from β-diketone vibrations common to all of the complexes. The frequency of these bands is fairly constant and their presence supports the proposition that the chelate ring structure for all of the compounds is identical with that of a normal β-diketone complex. It is worthwhile to mention the assignment of the two strong absorptions in the 1500–1600-$\mathrm{cm^{-1}}$ region. The 1570-$\mathrm{cm^{-1}}$ band is assigned to primarily a carbonyl stretching motion while the 1520-$\mathrm{cm^{-1}}$ absorption is assigned to a carbon–carbon stretching vibration of the chelate ring. The reverse designation was made on the basis of a normal coordinate analysis.[16] However, a recent infrared spectral study with oxygen-18-labeled acetylacetone coordination compounds is not in agreement with the latter analysis.[19] In fact, the isotope shifts confirm the assignment used here and elsewhere.[20]

The infrared spectra allow a differentiation to be made between the three types of complexes. For instance, only complexes where the nitrite ion is present, $\mathrm{[Co(dik)_2(NO_2)_2]^-}$ and $\mathrm{[Co(dik)_2NO_2py]}$, show the strong $\mathrm{NO_2^-}$ absorptions at ~1440, ~1310, and ~820 $\mathrm{cm^{-1}}$. These absorptions can be assigned to the $\mathrm{NO_2^-}$ antisymmetric stretch, symmetric stretch, and bending mode, respectively. The frequency of these bands also supports the conclusion that the nitrite ion is coordinated and is bound to the cobalt ion *via* the nitro-

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(17) J. M. Rigg and E. Sherwin, *J. Inorg. Nucl. Chem.*, **27**, 653 (1965).

(18) K. Nakanishi, "Infrared Absorption Spectroscopy," Holden-Day, Inc., San Francisco, Calif., 1962.

(19) S. Pinchas, B. L. Silver, and I. Laulicht, *J. Chem. Phys.*, **46**, 1506 (1967).

(20) L. J. Boucher and J. C. Bailar, Jr., *Inorg. Chem.*, **3**, 589 (1964).

gen atom and not the oxygen atom.[21] Unfortunately the pyridine C=C, C=N stretching absorptions are not readily observed because of their overlap with the strong β-diketone bands in the 1500–1600-cm^{-1} region. The latter materials do, however, show medium-intensity absorptions at 780 and 705 cm^{-1} which arise from the pyridine ring hydrogen deformations. Finally only the ethylenediamine complexes show $-NH_2$ stretching absorptions at 3100–3200 cm^{-1}.

Nuclear magnetic resonance spectra of $[Co(dik)_2NO_2py]$ in $CDCl_3$ and of $[Co(dik)_2en]I$ in D_2O have been determined. Proton chemical shifts are listed in Table III. The assignments are based on those first given for acetylacetone complexes[22] and organic compounds.[23] The spectra are of considerable value in characterizing the various coordination compounds. All of the spectra show a low-field resonance at -6.0 to -5.3 ppm which can be assigned to the methine proton of the enolate anion. Likewise, the complexes show a methyl proton resonance at -2.1 to -2.2 ppm (methyl group directly attached to the carbonyl carbon). The methoxyacetylacetone complexes show resonances at -3.3 to -3.5 and -4.0 to -4.1 ppm for the methyl and methylene protons of the ether group. The oxygen atom deshields both sets of protons in this case. The assignment is supported by the integrated intensities of the peaks which give the expected 3:2 ratio. The spectra of the propionylacetone complexes show the typical ethyl pattern of proton resonances: a methylene quartet at -2.1 to -2.7 ppm and methyl triplets at -1.3 to -0.9 ppm with a proton coupling constant of ~7 cps. While the enolate anion effectively deshields the methylene protons, the methyl protons are only slightly affected.

Table III

Nuclear Magnetic Resonance Spectra of Complexes

$[Co(dik)_2NO_2py]$[a]			$[Co(dik)_2en]I$[b]			
acac	mcac	prac	acac	macac	prac	Assignment
-5.33[c]	-5.72	-5.35	-5.82	-5.92	-5.78	C–*H*
	-4.05			-4.16		–C*H*$_2$O
				-4.14		
	-3.32			-3.43		–O–C*H*$_3$
				-3.35		
		-2.58			-2.67	–C*H*$_2$–CH$_3$
		-2.54			-2.60	
		-2.44			-2.55	
		-2.42			-2.48	
					-2.42	
		-2.31			-2.35	
		-2.18			-2.30	
					-2.23	
-2.12	-2.20	-2.13	-2.18	-2.24	-2.16	–C*H*$_3$
	-2.18			-2.22	-2.15	
					-2.14	
		-1.23			-1.23	–C*H*$_2$–CH$_3$
					-1.20	
		-1.09			-1.12	
		-1.08			-1.08	
					-1.00	
		-.096			-0.95	

[a] 10% (w/v) in $CDCl_3$; chemical shifts relative to tetramethylsilane (1–2%) internal standard. [b] 5% (w/v) in D_2O; chemical shifts relative to sodium 3-trimethylsilyl-1-propanesulfonate internal standard, 2% (w/v). [c] Ppm.

The $[Co(dik)_2NO_2py]$ complexes show pyridine ring proton resonances at -7.2 to -8.0 ppm. Also, the ethylenediamine complexes show a single unresolved methylene proton resonance at -2.75 ppm. This suggests that conformational interchange of the ethylenediamine chelate ring is rapid.[24] Within each series of compounds there is not a discernible shift of these resonances (nor the common methyl group either). There is, however, a consistent diamagnetic shift of the proton resonance in going from the nitropyridine complex to the ethylenediamine complex. The alkyl proton resonances are only very slightly affected and the observed difference may be due to a solvent effect. Conversely the methine proton shows a large shift (0.2–0.5 ppm) which cannot be rationalized in this way. Both $[Co(acac)_2(NH_3)_2]^+$ and $[Co(acac)_2(NO_2)_2]^-$ show a *trans* to *cis* diamagnetic shift of <0.1 ppm. The shift observed here is probably a consequence of the coordinated pyridine molecule and the magnetic anisotropy associated with its ring current. This is supported by the observation that both the *cis*-dipyridine and bipyridinebis(acetylacetonato)cobalt(III) salts show methine proton resonances at approximately the same position[9] as those reported here for the pyridine complexes.

In summary, then, the ultraviolet, visible, infrared, and nuclear magnetic resonance spectral properties of the materials reported here are entirely consistent with the formulations given. In addition, the closely similar chemical properties and syntheses of the complexes for all three β-diketones lend support to the notion of a common structure for each type of complex.

Stereochemistry.—Both the $[Co(dik)_2(NO_2)_2]^-$ salts and the $[Co(dik)_2NO_2py]$ complexes can exist as either *cis* or *trans* geometrical isomers. Many spectral methods have been devised to differentiate such isomer pairs. The high-symmetry *trans* isomer is expected to have fewer spectral lines than the low-symmetry *cis* isomer. In addition, spectral line shifts can be related to a change in geometry. The rules are extremely useful if the two isomeric materials are at hand. However, the isolation of only one isomer makes the assignment of its configuration tentative at best. The situation is somewhat less dissatisfying if data are available for closely related compounds.

Two isomers of $[Co(acac)_2(NO_2)_2]^-$ have now been isolated. The first isomer was reported by Rosenheim and Garfunkel and was prepared by the method of reaction 1. A second isomer has recently been synthesized, using a different method, by Cotsoradis and Archer.[7] Although the electronic spectra of the complexes are nearly identical, their infrared and nmr spectra are significantly different. Infrared spectroscopy has been used to establish the identity of *cis*- and *trans*-

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(21) K. Nakamoto, J. Fujita, and H. Murata, *J. Am. Chem. Soc.*, **80**, 4817 (1958).

(22) R. H. Holm and F. A. Cotton, *ibid.*, **80**, 5658 (1958).

(23) L. M. Jackman, "Applications of Nuclear Magnetic Resonance in Organic Chemistry," Pergamon Press Ltd., London, 1959.

(24) D. A. Buckingham, L. Durham, and A. M. Sargeson, *Australian J. Chem.*, **20**, 257 (1967).

dinitrocobalt(III) salts.[25] The *cis* isomers show a splitting of the NO_2^- symmetric stretching band (near 1340 cm^{-1}) and the NO_2^- bending absorption (near 820 cm^{-1}) while the corresponding *trans* isomers show only a single band in each of these regions. The infrared spectrum of the Rosenheim isomer of $[Co(acac)_2(NO_2)_2]^-$ has only single nitro absorptions at 1308 and 824 cm^{-1}. On the other hand, the second isomer has two bands in each of these regions at 1340, 1315 and 832, 840 cm^{-1}, respectively.[7] This leads to the assignment of a *trans* configuration to the Rosenheim isomer and a *cis* configuration to the other isomer. The infrared spectra of the $[Co(dik)_2(NO_2)_2]^-$ salts with methoxyacetylacetone and propionylacetone show only single strong absorption at 1309 and 825 cm^{-1} for the NO_2^- symmetric stretching and bending modes, respectively. This is consistent with a *trans* configuration for these ions. The common syntheses and reactions of the materials with *trans*-$[Co(acac)_2(NO_2)_2]^-$ also support the notion of a common configuration. The second isomer of the dinitro complexes reported here has not, as yet, been prepared. Confirmation of the suggested assignments awaits isolation (and observation of spectral properties) of the other isomer.

The designation of the *cis*- and *trans*-$[Co(acac)_2(NO_2)_2]^-$ isomers has been confirmed by the proton magnetic resonance spectral properties of the two materials. The nmr spectra can be predicted on the basis of an empirical observation first exploited by Piper and Fay.[5] They observed that, for unsymmetrical β-diketone complexes, protons which are not related to each other by some symmetry element will generally show different chemical shifts. By far, the largest differences are observed for the methyl protons of the enolate anion. The differences in methine proton chemical shifts are usually small. The origin of the chemical shift variation in these complexes is still a matter of discussion.[26]

In the case of $[Co(acac)_2(NO_2)_2]^-$ the empirical nmr rule holds. In the *trans* isomer all four methyl groups are equivalent; this yields only one observed methyl proton resonance. Similarly, for the *cis* isomer there are two different sets of methyl groups; this gives rise to two observed methyl proton resonances. Although the methine proton resonance is at lower field for the *cis* isomer, only a single line was seen for each isomer. The same methyl proton pattern is observed for *cis*- and *trans*-$[Co(acac)_2(NH_3)_2]^+$.[8] The only example definitely contrary to the nmr rule is the $[Co(acac)_2en]^+$ ion. Although this compound must have a *cis* configuration, only one methyl proton resonance is observed. Lability and rapid exchange of the acetylacetone ligand cannot account for this since the optically active ion is stable to racemization for days at room temperature in aqueous solution.[27]

The nmr spectrum of $[Co(acac)_2NO_2py]$ shows only a single methyl proton resonance. This is consistent with a *trans* configuration for the complex. The *cis* isomer would have four nonequivalent methyl groups and its nmr spectrum should show as many as four methyl proton resonances. Degenerate nmr peaks would seem unlikely in this case since the anionic nitro ligand should enhance the nonequivalence of methyl groups. The presence of the pyridine ligand with its magnetic anisotropy would also have the same effect. The ultraviolet–visible and infrared spectra of $[Co(macac)_2NO_2py]$ and $[Co(prac)_2NO_2py]$ are very similar to those of $[Co(acac)_2NO_2py]$. Also, all three ions were prepared from the rapid reaction of *trans*-$[Co(dik)_2(NO_2)_2]^-$ with pyridine. There is no reason to suspect then that all of the complexes would not have the same configuration.

If the $[Co(dik)_2NO_2py]$ complexes are assumed to have a *trans* configuration, with respect to the monodentate ligands, the compounds with unsymmetrical β-diketones can exist as two additional geometrical isomers. These are analogous to the edge and facial isomers of the tris(unsymmetrical β-diketone) metal complexes. The two forms which are designed "*cis*" and "*trans*" with respect to the R group of the β-diketone are shown in Figure 1. The same type of stereoisomerism must exist for the *trans*-$[Co(dik)_2(NO_2)_2]^-$ ions. Both the "*cis*" and "*trans*" isomers each have a set of equivalent methyl groups and a set of equivalent R groups. However, the methyl (and R) groups in the "*cis*" isomer are not equivalent to the methyl groups in the "*trans*" isomer. Therefore, the two isomers could give rise to different nmr spectra; *i.e.*, "*cis*" methyl protons, would have a chemical shift slightly different from that of a "*trans*" methyl proton, etc. The nmr spectrum of $[Co(macac)_2NO_2py]$ does, in fact, show two methyl proton resonances of approximately equal intensity. The ether and methine resonances show only one resonance. The methylene line is, however, rather broad (half-width at half-height ~3.5 cps). Similarly, the nmr spectrum of $[Co(prac)_2NO_2py]$ shows six lines for the methylene group and four lines for the methyl group. The six methylene proton resonances arise from the incomplete resolution of two quartets and the four methyl resonances arise from the incomplete resolution of the two triplets. No splitting is seen for the methyl or methine resonance. The nmr data indicate that both the $[Co(dik)_2NO_2py]$ complexes examined are mixtures of two species in nearly equal concentration. The two species are probably the isomers pictured in Figure 1. Another explanation is that the two materials are the more conventional *cis* and *trans* isomers (with respect to the monodentate ligands). The relatively small chemical shift differences between the two species argue against this. So does the observation of only one relatively narrow (half-width ~1 cps) methine proton resonance. The methine proton chemical shift differs by at least 0.04 ppm for similar *cis–trans* isomer pairs.[7]

The $[Co(dik)_2en]^+$ cations necessarily have a *cis* configuration. The complexes of unsymmetrical β-diketones can exist as any of three possible geometrical

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[25] (a) M. Lepostallec, J. P. Mathieu, and H. Poulet, *J. Chim. Phys.*, **60**, 1319 (1963); (b) B. M. Gatehouse, *J. Inorg. Nucl. Chem.*, **8**, 79 (1958).

[26] J. P. Collman, *Angew. Chem. Intern. Ed. Engl.*, **4**, 132 (1966).

[27] L. J. Boucher, unpublished results.

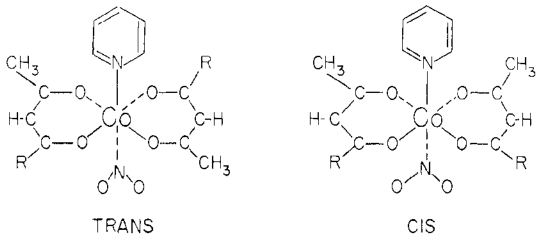

Figure 1.—Geometrical isomers of *trans*-nitropyridinebis(β-diketonato)cobalt(III); R = CH_2CH_3 or CH_2OCH_3.

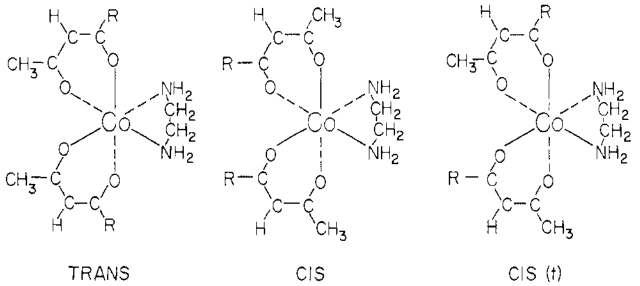

Figure 2.—Geometrical isomers for the ethylenediaminebis(β-diketonato)cobalt(III) cation; R = CH_2CH_3 or CH_2OCH_3.

forms[6] (in addition to their three optical antipodes). The isomers are displayed in Figure 2. The "*cis*" and "*trans*" isomers both have a set of equivalent methyls while the "*cis*" (t) isomer has nonequivalent methyl groups (and R groups). The chemical shifts of the methyl protons could be different in each case. The nmr spectrum could then show four methyl resonances for a mixture of the three isomers.[28] The nmr spectrum of $[Co(macac)_2en]^+$ shows two clearly resolved resonances each for the ether methyl and methylene protons as well as for the methyl protons. Each pair of lines shows approximately a 3:2 intensity ratio. This latter point rules out the possibility of the material being the pure "*cis*" (t) isomer since the ratio in this case would be 1:1. The nmr spectrum of $[Co(prac)_2en]^+$ shows a complex pattern of lines. There are at least two superimposed ethyl patterns and the methyl proton resonance shows three values. For both $[Co(dik)_2en]^+$ ions the methine proton resonances are not split. The above data are consistent with the notion that the materials examined are a mixture of the three possible isomers. The distribution should be close to statistical since there should be very little free energy difference between them.[6] It is interesting to note that there is apparently a substantial difference in chemical shifts for methyl protons exclusively *cis* to the ethylenediamine and for methyl protons *trans* to it. This is not observed for $[Co(acac)_2en]^+$. The reason for this may involve the differing steric interactions of the ethyl and methoxymethyl groups as opposed to a methyl group. Further comment on these very interesting isomers must await their separation and individual characterization. Work of this sort is in progress.

Acknowledgment.—Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

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Contribution from the Department of Chemistry,
The University of Rome, Rome, Italy

The Stepwise Base Hydrolysis of *cis*- and *trans*-Diacetatobis(ethylenediamine)cobalt(III) Ions[1]

By VINCENZO CARUNCHIO, GABRIELLO ILLUMINATI, and GIANCARLO ORTAGGI

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Our previous knowledge on the stepwise hydrolysis of *cis*- and *trans*-diacetatobis(ethylenediamine)cobalt(III) ions is complemented by the determination of the kinetics of the reaction of the intermediate acetatohydroxo complexes and by a study of the stereochemical course. In both *cis* and *trans* configurations the second step is found to be slower than the first one. Also, a nearly complete *trans* → *cis* change is observed in the second step, while *cis* or *trans* configurations are retained in the other cases. The results are compared with several other data of the same type of reactions and are found to be consistent with a dissociative mechanism.

Introduction

Previous work[2] has dealt with the base hydrolysis of the first functional group of dicarboxylato complexes of the general type $Co(en)_2(OCOR)_2^+$, the R groups being of widely different structure. It seemed of interest, at least in one typical case, to consider the reaction of the second functional group for a more complete picture of the reaction kinetics. In this paper we report some observations on the kinetics and stereochemical course of the consecutive base hydrolysis reactions of the *cis*- and *trans*-diacetato complexes as described by eq 1 and 2.

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[1] (a) Structure and Reactivity in Octahedral Complexes. Part IX; (b) Previous paper in this series: G. Illuminati and F. Monacelli, *J. Inorg. Nucl. Chem.*, in press.

[2] V. Carunchio, G. Illuminati, and F. Maspero, *ibid.*, **28**, 2693 (1966).