shielding to the two protons on the G ring. In the R rings, H_a and H_b appear to be symmetrically oriented with respect to the carbonyl, and no net effect of this group on the protons would be expected.

The [Co(EDTA)]$^-$ Spectrum.—Day and Reilley[9] studied the n.m.r. spectrum of [Co(EDTA)]$^-$ which is summarized in Table IV.[31] They assigned the AB spectrum with only a small chemical shift to the R ring and the spectrum with a larger chemical shift to the G ring. This same assignment would be anticipated in terms of the anisotropy of the C–N bonds. It is interesting to compare differences between [Co(EDTA)]$^-$ and *cis*-[Co(en)(EDDA)]$^-$ to the differences between *trans*-[Co(en)(EDDA)]$^+$ and *trans*-[Co(en)(DEEDDA)]$^+$. In the latter case H_a is shifted upfield by 0.09 p.p.m. and H_b is shifted downfield by 0.25 p.p.m. on the addition of alkyl substitution. The spectra of *cis*-[Co(en)(EDDA)]$^+$ and [Co(EDTA)]$^-$ appear to be similarly related as summarized in Table V. This interesting correlation tends to confirm the assignments of *cis*-[Co(en)(EDDA)]$^+$ and [Co(EDTA)]$^-$ and suggests that the anisotropic effects for these various complexes are similar.

TABLE V

COMPARISON OF CHEMICAL SHIFTS OF *cis*-[Co(en)(EDDA)] AND [Co(EDTA)]$^+$

	R ring		G ring	
	δ_a	δ_b	δ_a	δ_b
cis-[Co(en)(EDDA)]$^+$	4.02	3.62	3.71	3.71
Obsd. [Co(EDTA)]$^-$ spectrum	3.96	3.88	3.59	3.91
Shift on alkyl substitution	−0.06	+0.26	−0.12	+0.20

Finally, by analogy with the n.m.r. spectra of the *trans* isomers the E ring of [Co(EDTA)]$^-$ should exhibit an A_2B_2 spectrum. Examination of the spectrum reveals a symmetrical set of lines superimposed on the two AB spectra of [Co(EDTA)]$^-$. The integration values are in good agreement with the assignments, Table III. The average chemical shift of 3.61 p.p.m. is less shielded than the 3.10 p.p.m. found for the corresponding E ring in *trans*-[Co(en)(EDDA)]$^+$. This indicates that the opening up of the C–N–C bond on coordination of the G acetate group results in a positioning of the E ring protons in a region of deshielding.

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[31] The spectrum that we list is the compilation of several measurements on our instrument over several months time using different samples of complex and standard. A comparable spectrum was obtained on the 60-Mc. instrument at the University of Pittsburgh using their sample and standard for which we thank Miss M. Gordon. Although Day and Reilley list no tabulation of numbers, our spectrum appears to be uniformly displaced 0.30 p.p.m. upfield from theirs, although we presumably are using the same standard. Although we are unable to explain this displacement in the spectra, the numbers that we obtain for [Co(EDTA)]$^-$ and our complexes are consistent within themselves.

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β-Diketone Complexes of Cobalt(III). I. Synthesis and Spectroscopy of Bis(acetylacetonato)diaminecobalt(III) Salts[1]

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The first known *cis*-[$Co^{III}(acac)_2L_2$]$^{x\pm}$ complexes have been prepared and studied by proton n.m.r., infrared, visible, and ultraviolet spectroscopy. The proton n.m.r. spectra of these stable complexes amplify the caution necessary in assigning coordination compound configurations based on chemical shifts—the [$Co(acac)_2(en)$]$^+$ ion, necessarily of *cis* configuration, exhibits only one sharp methyl resonance peak even though two are predicted. Salts of the ethylenediamine complex, of [$Co(acac)_2(bipy)$]$^+$, of [$Co(acac)_2(py)_2$]$^+$, and of *cis*- and *trans*-[$Co(acac)_2(NH_3)_2$]$^+$ have been synthesized using carbon as a catalyst.

Introduction

Whereas most cobalt(III) complexes that have been studied undergo substitution reactions with a predominant retention of configuration, the D*-*cis*-dichlorobis(ethylenediamine)cobalt(III) ion reacts with ammonia[2] and hydroxide ion[3] to give mainly *trans* and L* products, where D* and L* indicate relative configurations.[2] Fragmentary studies with the corresponding chlorobromo and dibromo complexes[2,4] suggest that these species behave in a manner similar to the dichloro ion. These dihalo ions possess weaker ligand fields than any other complexes of the bis(ethylenediamine) series. Since members of the bis(β-diketone) series should have lower ligand field strengths than the corresponding ethylenediamine complexes,[5] and since the β-diketone

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[1] Amine is used herein to indicate any nitrogen electron-pair donor, whereas ammine is reserved for coordinated ammonia. Abbreviations used include: acac = anion of the enol form of 2,4-pentanedione (*i.e.*, acetylacetonate); bipy = 2,2′-bipyridine; en = ethylenediamine; py = pyridine; L = a unidentate ligand or one-half of a bidentate ligand; and x = the charge on the complex species.

[2] R. D. Archer, Proceedings of the Eighth International Conference on Coordination Chemistry, Vienna, 1964, pp. 111–114; R. D. Archer and J. C. Bailar, Jr., *J. Am. Chem. Soc.*, **83**, 812 (1961).

[3] L. J. Boucher, E. Kyuno, and J. C. Bailar, Jr., *ibid.*, **86**, 3656 (1964).

[4] J. C. Bailar, Jr., and D. F. Peppard, *ibid.*, **62**, 820 (1940); S. C. Chan and M. L. Tobe, *J. Chem. Soc.*, 4531 (1962).

[5] The $^1T_{1g}$ energy level of [$Co(acac)_3$] lies about 17,000 cm.$^{-1}$ above the $^1A_{1g}$ ground state compared to about 21,000 cm.$^{-1}$ for the [$Co(en)_3$]$^{3+}$ ion: C. K. Jørgensen, "Absorption Spectra and Chemical Bonding in Complexes," Pergamon Press, Oxford, 1962, and references cited therein.

complexes should not be subject to conjugate base reactions, we have begun a detailed study of the bis(β-diketone) complexes in order to check the effect of ligand field strength on reaction rates and stereochemistry in the absence of acidic protons.[6]

The salts of the $[Co(acac)_2(NO_2)_2]^-$ anion[7] were the only reported bis(acetylacetonato)complexes of cobalt(III) until Boucher and Bailar[8] prepared a series of nitrobis(acetylacetonato)aminecobalt(III) complexes by substituting numerous amines for one of the nitro groups in the dinitro complex. We also had observed this reaction independently. The other investigators[8] found no evidence for *cis* isomers or for substitution of the second nitro group by amines even in boiling amine solvents. Using an activated carbon catalyst in water, we have been able to prepare several bis(acetylacetonato)diaminecobalt(III) complexes including both the *cis* and the *trans* isomers of the diammine complex.

Results

Synthesis.—A series of bis(acetylacetonato)diaminecobalt(III) species has been isolated through the reaction of $[Co(acac)_2(NO_2)_2]^-$ with ammonia, ethylenediamine, pyridine, or bipyridine in the presence of activated carbon. The *cis*- and *trans*-$[Co(acac)_2(NH_3)_2]^+$ isomers have been separated on the basis of solubility differences. In order to attain sufficient solubility for the synthesis of the bipyridine derivative, a mixed solvent of methanol and water has been found essential. The mixed solvent also has been used for preparing the pyridine derivative. At room temperature these new complexes are stable in air and in the polar solvents used in this study; however, aqueous hydrochloric acid solutions decompose the complexes.

In the absence of charcoal the only product isolated after several minutes of standing was the mononitromonoamine derivative. The initial precipitate which forms upon the addition of aqueous ammonia to a concentrated solution of the dinitro complex has the composition of a mixture of the ammonium salt of the dinitro complex and the desired nitroammine complex.

Nuclear Magnetic Resonance Spectra.—The n.m.r. spectra for all of the new complexes are reported in Table I. The presence of two isomers of bis(acetylacetonato)diamminecobalt(III) iodide was first noted from the n.m.r. spectrum of the mixture prepared as cited in the Experimental section. Two approximately equal CH resonance peaks at -5.78 and -5.68 p.p.m. and two unequal (*ca.* 3:1) methyl resonance peaks at -2.16 and -2.18 p.p.m. were observed for the mixture. This indicated the presence of two isomers of the diammine complex in about equal amounts. Subsequent separation of the isomers confirmed this observation.

TABLE I

PROTON CHEMICAL SHIFTS FOR BIS(ACETYLACETONATO)COBALT(III) COMPLEXES

Complex	Methyl protons Peak position[a]	Methyl protons Half-width[b]	CH protons Peak position[a]	CH protons Half-width[b]
$[Co(acac)_2(bipy)]I$[c]	-1.93 (3)	0.03_2	-5.32 (1)	0.02
	-2.40 (3)	0.03_2		
$[Co(acac)_2(en)]ClO_4$[d,e,f]	-2.25 (6)	0.02_0	-5.80 (1)	0.02
$[Co(acac)_2(py)_2)I$[c]	-2.18 (6)	0.02_5	-5.32 (1)	0.02
cis-$[Co(acac)_2(NH_3)_2]I$[d]	-2.16 (3)	*g*	-5.78 (1)	0.02
	-2.18 (3)	*g*		
trans-$[Co(acac)_2(NH_3)_2]I$[d]	-2.18 (6)	0.02_7	-5.68 (1)	0.02

[a] Chemical shifts in p.p.m. relative to tetramethylsilane (unless otherwise noted). Relative integrated intensities are indicated in parentheses. [b] Half-width at half-height in p.p.m. [c] Saturated solution in $CDCl_3$. [d] D_2O as solvent. [e] DOH used as reference. [f] Also shows peak for ethylenediamine CH_2 groups at -2.75 p.p.m. with half-width of 0.04 p.p.m. [g] Peaks are not fully resolved.

TABLE II

CHARACTERISTIC INFRARED SPECTRAL PEAKS OF SEVERAL $[Co(acac)_2L_2]X$ COMPLEXES[a,b]

L₂: *trans*-$(NH_3)_2$	*cis*-$(NH_3)_2$	en	bipy	py_2	Assignment
3120 m	3100 m	3240 m			N—H stretch
1575 s	1568 s	1575 s	1555 s	1545 s	C$\cdots$C stretch
1525 s	1518 s	1528 s	1524 s	1518 s	C$\cdots$O stretch
			1452 m	1442 m	py ring vibration
1425 sh	1420 sh		1423 m	1421 m	acac combination[c]
1380 s	1374 s	1378 s	1368 s	1371 s	CH_3 deformation
			1305 m	1330 m	
1290 m	1280 m	1280 m	1275 m	1283 m	acac combination[c]
				1068 m	py ring vibration
1020 m	1016 m	*d*	1029 m	1031 m	CH_3 rock
945 m	939 m	938 m	945 m	948 m	acac combination[c]
			840 m[e]	815 m	ring H(py), out-of-plane bending
			804 m[e]		
790 m					
775 m	773 m	769 m	764 s	762 s	ring H(acac), out-of-plane bending

[a] Iodide salts were measured for all but the en complex, for which the perchlorate salt was measured. [b] Spectral intensities: s, strong; m, medium; w, weak; sh, shoulder. Readings in cm.$^{-1}$. [c] *Cf.* ref. 9. [d] Peak is obscured by perchlorate absorption. [e] These peaks appear as one more intense peak at 825 cm.$^{-1}$ in amorphous samples.

Infrared Spectra.—The vibrational spectra of all the new complexes have been obtained in the region from 3500 to 700 cm.$^{-1}$. Table II lists the characteristic bands for these new complexes.

Assignments for the bands have been made by correlation with spectra of other complexes wherever possible. Assignments of the bands of the coordinated acetylacetonate ligand have been made with reference to a recent assignment of the vibrational bands in tris(acetylacetonato)cobalt(III) based on a normal coordinate analysis.[9] Assignment of the pyridine vibrational modes has been made with reference to the assignment of some other pyridine–metal ion complexes[10] and similarly the assignment of the vibrational modes of the bipyridine complexes has been made by correlation with the assignments of the tris(2,2′-bipyridine)cobalt(III) ion.[11] Assignment of the various vibrational modes of the ammonia and the ethylenedi-

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(6) Several studies on the higher ligand field complexes, $[Co(bipy)_2L_2]^{x+}$, have been reported; *e.g.*, R. G. Pearson, R. E. Meeker, and F. Basolo, *J. Inorg. Nucl. Chem.*, **1**, 341 (1955); F. Basolo, J. G. Bergmann, R. E. Meeker, and R. G. Pearson, *J. Am. Chem. Soc.*, **78**, 2676 (1956); V. Caglioti and G. Illuminati, Proceedings of the Eighth International Conference on Coordination Chemistry, Vienna, 1964, pp. 293–296.

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

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(10) N. S. Gill, R. H. Nuttall, D. E. Scaife, and D. W. A. Sharp, *J. Inorg. Nucl. Chem.*, **18**, 79 (1961).

(11) A. A. Schilt and R. C. Taylor, *ibid.*, **9**, 211 (1959).

TABLE III

VISIBLE AND ULTRAVIOLET SPECTRA OF SEVERAL $[Co(acac)_2L_2]X$ COMPLEXES[a]

	L_2				
	py_2	*trans*-$(NH_3)_2$	*cis*-$(NH_3)_2$	en	bipy
X	ClO_4	Cl	Cl	ClO_4	ClO_4
Solvent	CH_3OH	H_2O	H_2O	H_2O	CH_3OH
$^1A_{1g} \rightarrow {}^1T_{1g}$	534 (1.94)	540 (1.89)	546 (2.12)	538 (2.20)	553 (2.19)
$t_{2g} \rightarrow \pi^*$(acac)	342 (3.74)	330 (3.86)	322 (3.85)	325 (3.90)	340 (3.54)[b]
$t_{2g} \rightarrow \pi^*$(py)					310 (4.26)[b]
$t_{2g} \rightarrow \pi^*$(py)	294 (4.08)				294 (4.30)
$\pi \rightarrow \pi^*$(acac)		250 (4.32)	246 (4.32)	244 (4.43)[b]	255 (4.47)[b]
$\pi \rightarrow \pi^*$(acac)	229 (4.69)	222 (4.54)	218 (4.49)	221 (4.54)	225 (4.73)

[a] All peak positions are given in mμ with the molar extinction coefficient logarithmic values given in parentheses. [b] Shoulder, mμ only approximate.

amine ligands has been made with reference to the discussion by Nakamoto[12] and the work on various ethylenediamine complexes by Powell and Sheppard.[13]

The infrared spectrum of the starting material, sodium dinitrobis(acetylacetonato)cobaltate(III), was obtained for both the dry and hydrated complex, $Na[Co(acac)_2(NO_2)_2]\cdot 5H_2O$.[7] The infrared spectrum of the dry complex agrees well with the bands recently reported by Boucher and Bailar.[8] However, the hydrated species shows an extra band at about 1325 cm.$^{-1}$ (which is only a slight shoulder in the dried complex) and a doublet (830 and 823 cm.$^{-1}$) rather than the singlet (822 cm.$^{-1}$) observed in the dried sample.

Absorption Spectra.—The absorption peaks in the visible and ultraviolet spectral regions for the complexes indicated are listed in Table III. The assignments have been made on the basis of previous interpretations.[5,8] 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. No difference was noted in the shape of the visible peak for the *cis* and *trans* diammine complexes.

Discussion

Nuclear Magnetic Resonance Spectra.—The assignment of a definite configuration to one of two or more possible isomers based on the lack of splitting of an n.m.r. resonance peak (or infrared-sensitive vibrations, see below) is questionable. Whereas Piper and coworkers[14] have noted separate proton n.m.r. peaks or a significant broadening in each case in which more than one peak is expected for inert tris(β-diketone) complexes, the proton n.m.r. spectrum of the inert $[Co(acac)_2(en)]^+$ complex with nonequivalent methyl groups only has one sharp methyl peak (Table I). This single, sharp peak was observed for solutions of the ethylenediamine complex in both D_2O and CH_3OD. The half-width of this peak is less than that of any of the other complexes of this study or of the mononitromonoamine complexes assigned a *trans* configuration by Boucher and Bailar.[8] On the other hand, the corresponding 2,2′-bipyridine derivative has two widely separated methyl resonance peaks (Table I), as expected. Models of the two complexes show a close proximity between two of the four acetylacetonate methyl groups and bipyridine in the latter complex, whereas all atoms of the ethylenediamine ligand are widely separated from all four of the methyl groups in the other complex. Furthermore, the methyls of the two β-diketone residues do not appear to be in close proximity with each other. This steric difference suggests that the solvation of all four methyl groups could be equivalent in the ethylenediamine complex, but that two distinct solvation patterns should exist for the bipyridine complex. The large separation in the chemical shifts of the nonequivalent methyl groups in the bipyridine complex may also be a result of the diamagnetic anisotropy associated with the ring current of the bipyridine ligand as suggested by Collman[15] to account for the chemical shifts in some complexes with three β-diketone ligands per metal atom. The methyl groups *trans* to each other in $[Co(acac)_2(bipy)]^+$ lie almost above the π-cloud of the nitrogen heterocyclic ligand at a distance of about 4 Å. and could be slightly shielded. On the other hand, the two *cis* methyl groups could be deshielded as a result of lying close to the bipyridine ligand and in the plane of the ligand. This anisotropy is in addition to that associated with the β-diketone rings. In order to explain the equivalent methyl resonance phenomenon for $[Co(acac)_2(en)]^+$ in this manner, a consideration of the geometry of the complex indicates that the anisotropy of the ethylenediamine ligand must be similar to that of the β-diketone ring, which seems unlikely.

Lability cannot account for the single peak in the ethylenediamine complex, although this effect is important in aluminum chelates of β-diketones.[14,16] More confidence could be placed in the above results if all of the species were soluble enough to observe n.m.r. spectra in a single solvent. On the other hand, methyl groups are even better separated in basic solvents than in $CDCl_3$ for some polar compounds.[17] Therefore, it is doubtful that splitting of the methyl resonance peak

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(12) K. Nakamoto, "Infared Spectra of Inorganic and Coordination Compounds," John Wiley and Sons, Inc., New York, N. Y., 1963, pp. 143–151, and references therein.

(13) D. B. Powell and N. Sheppard, *Spectrochim. Acta*, **17**, 68 (1961).

(14) R. C. Fay and T. S. Piper, *J. Am. Chem. Soc.*, **84**, 2303 (1962); *ibid.*, **85**, 500 (1963); R. C. Fay and T. S. Piper, *Inorg. Chem.*, **3**, 348 (1964); R. A. Palmer, R. C. Fay, and T. S. Piper, *ibid.*, **3**, 875 (1964).

(15) J. P. Collman, R. L. Marshall, and W. L. Young, III, *Chem. Ind.* (London), 1380 (1962); J. P. Collman, R. L. Marshall, and W. L. Young, III, Proceedings of the Seventh International Conference on Coordination Chemistry, Stockholm, 1962, pp. 55, 56.

(16) R. E. Sievers and R. G. Linck, private communication.

(17) G. Slomp and F. MacKellar, *J. Am. Chem. Soc.*, **82**, 999 (1960).

for the ethylenediamine complex would be observed in the less polar solvents since it is not observed in D_2O or CH_3OD.

Only a very slight splitting (0.02 p.p.m.) exists between the nonequivalent methyl groups in the *cis*-$[Co(acac)_2(NH_3)_2]^+$ ion. The *trans* complex only has one methyl resonance peak, as expected. A molecular model of the *cis* complex also suggests the possibility of approximately equivalent solvation for all methyl protons.

Equal chemical shifts for the nonequivalent protons in the ethylenediamine complex eliminates the possibility of a definite assignment for the pyridine derivative. The bulky nature of this heterocyclic ligand suggests that unequal solvation is probable, so the single methyl resonance *probably* implies a *trans* configuration. Similar arguments can be made for the assignments made by Boucher and Bailar.[8]

Infrared Spectra.—Although *cis* isomers normally have more infrared-active absorption peaks because of low symmetry,[18] the use of peak multiplicity in assigning a *cis* or *trans* configuration when only one isomer has been isolated should be avoided whenever possible. Configurations assigned in this way must be considered only tentative. For example, although anhydrous Na$[Co(acac)_2(NO_2)_2]$ has only a single infrared-active peak attributable to the nitro group in either the 800 or 1300 cm.$^{-1}$ region and has therefore been assigned a *trans* configuration,[8] the present investigation has noted a double absorption in both regions for the hydrated species. Furthermore, the pyridine and 2,2′-bipyridine derivatives each have absorption peaks just above 800 cm.$^{-1}$, the multiplicity of which varies with environment. Amorphous $[Co(acac)_2(bipy)]^+$ has only one peak in this region, whereas the crystalline sample has two distinct peaks. (These absorptions are attributable to out-of-plane vibrations of the ring hydrogens of the nitrogen heterocycles.[10,11]) Also, whereas the *cis*-$[Co(acac)_2(NH_3)_2]^+$ and $[Co(acac)_2(en)]^+$ ions of low symmetry only exhibit a single, intense band in the 760–800 cm.$^{-1}$ region, the more symmetrical *trans*-$[Co(acac)_2(NH_3)_2]^+$ ion has two fairly strong peaks in this region. This example is the most striking since the *trans* isomer (rather than the less symmetrical *cis* isomer) appears to have the more complex spectrum.

Visible and Ultraviolet Spectra.—The *cis* isomer of the diamine salts and the isomers which result from the chelated ligands all possess similar molar extinction coefficients. Approximately equal but somewhat lower values have been observed for the *trans*-diammine and for the dipyridine complex. Interestingly, the corresponding monoamine chelates[8] show intermediate values, suggestive of *trans* isomers of lower symmetry than the disubstituted derivatives. However, some *cis* isomers do have lower extinction coefficients than the corresponding *trans* isomers in other cobalt(III) complexes.[19] All in all, evidence for a *trans* configuration for the dipyridine derivative of this study as well as the monoamine complexes[8] is quite compelling.

Synthesis.—Whereas $[Co(acac)_2(NO_2)_2]^-$ normally reacts with amines in aqueous solution to give only the mononitromonoamine species, activated carbon catalysis has allowed the isolation of several diamines. Activated carbon has been used as a catalyst for cobalt(III) complexes for several years,[20] even though the exact manner in which it lowers activation energies is uncertain. The catalysis appears to be selective since we have observed further reaction upon standing; *e.g.*, $[Co(acac)_2(bipy)]^+$ in the presence of the released nitrite ions slowly reacts to form $[Co(acac)(NO_2)_2(bipy)]$.[21] Both the *cis* and *trans* isomers of the diamines appear to be quite stable in the absence of strong nucleophiles or strong acids.

Although the loss of only one nitro ligand has been ascribed to a *trans* effect, the resultant amines do not appear to exchange.[8] Kinetics studies in progress in our laboratories suggest that the reaction is not simply a direct reaction with the amine. No definite conclusions on the mechanism can be drawn at this time.

Experimental

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

Sodium Dinitrobis(acetylacetonato)cobaltate(III).—The complex was prepared from sodium hexanitrocobaltate(III) using the method of Rosenheim and Garfunkel.[7] To recrystallize the complex, the dissolved complex was filtered into a flask in an ice bath, and then a saturated solution of sodium nitrite slowly was added with stirring to the cold filtrate. This is similar to a procedure used by Boucher and Bailar.[8]

Norit A Carbon.—Two brands of Norit A decolorizing carbon were used, namely, Fisher Scientific Norit A decolorizing carbon and Pfanstiehl Norit A decolorizing carbon, without any apparent differences in the results.

Bis(acetylacetonato)dipyridinecobalt(III) Iodide.—Recrystallized sodium dinitrobis(acetylacetonato)cobaltate(III) (2.0 g., 5.4 mmoles) was dissolved in 50 ml. of cold water and 20 ml. of methanol. Then 1.5 g. of Norit A carbon was added, followed immediately by 3 ml. of pyridine (37 mmoles). The solution was stirred vigorously for 15 min. in a warm bath (*ca.* 50°). The solution was filtered by suction. The charcoal was washed twice with 5-ml. portions of methanol. The washings were combined with the red-brown filtrate. Subsequently 2.5 g. of sodium iodide (16 mmoles) dissolved in 5 ml. of water was added to the filtrate with stirring. The solution was allowed to cool in an ice bath and filtered. The precipitate was washed with two 5-ml. portions of ice water.

The brown-red precipitate was recrystallized by dissolution in a minimum amount of boiling methanol and filtration while hot. The solution was allowed to cool and then refiltered. The resulting precipitate was washed with small quantities of methanol and ether. Further complex was recovered by adding

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(19) F. Basolo, *J. Am. Chem. Soc.*, **72**, 4393 (1950).

(20) J. B. Work, Ph.D. Thesis, University of Illinois, 1942; B. E. Douglas, *J. Am. Chem. Soc.*, **76**, 1020 (1954); F. P. Dwyer and A. M. Sargeson, *Nature*, **187**, 1022 (1960); J. A. Broomhead, F. P. Dwyer, and J. W. Hogarth, *Inorg. Syn.*, **6**, 186 (1960); H. E. Swift and B. E. Douglas, *Nature*, **193**, 1173 (1962); W. C. Erdman and B. E. Douglas, *J. Inorg. Nucl. Chem.*, **24**, 1355 (1962); W. C. Erdman, H. E. Swift, and B. E. Douglas, *ibid.*, **24**, 1365 (1962); H. E. Swift and B. E. Douglas, *ibid.*, **26**, 601 (1964); B. E. Douglas and S. M. Ho, *ibid.*, **26**, 609 (1964).

(21) B. P. Cotsoradis and R. D. Archer, unpublished results.

5 ml. of ether to the methanol filtrate and removing the precipitated product by filtration; total yield 1.0 g., 34%.

Anal. Calcd. for $C_{20}H_{24}O_4N_2CoI$: C, 44.28; H, 4.43; N, 5.17. Found[22]: C, 43.58; H, 4.42; N, 5.11.

Bis(acetylacetonato)dipyridinecobalt(III) Perchlorate.—The initial procedure for the formation of the dipyridine complex in the presence of carbon was identical with the procedure for preparing bis(acetylacetonato)dipyridinecobalt(III) iodide. After filtering the solution to remove the carbon, 1.0 g. of sodium perchlorate monohydrate (7.1 mmoles) dissolved in 3 ml. of water was added to the filtrate. A precipitate appeared immediately. The solution was allowed to cool and then filtered.

The product was recrystallized by dissolving the precipitate in a minimum amount of boiling methanol and filtering the hot solution. Upon cooling, 10 ml. of ether was added to the filtrate. The solution was then chilled in an ice bath and refiltered. The golden brown precipitate was washed with several small portions of methanol and ether; total yield of recrystallized product 0.73 g., 26%.

Bis(acetylacetonato)ethylenediaminecobalt(III) Perchlorate.—Recrystallized sodium dinitrobis(acetylacetonato)cobalt(III) (2.0 g., 5.4 mmoles) was dissolved in 50 ml. of cold water and 10 ml. of methanol. Then 1.0 g. of Norit A carbon and 0.34 g. of ethylenediamine (5.7 mmoles) in 10 ml. of water were added to the solution of the complex. The solution was stirred vigorously for 10 min. at room temperature. The mixture was filtered by suction, and the carbon was washed with two 5-ml. portions of water. The washings were combined with the violet filtrate, after which 15 g. of sodium perchlorate monohydrate (110 mmoles) dissolved in 15 ml. of water was added. The solution was allowed to cool and then filtered. The violet crystals were washed with 5 ml. of ice water.

The product was recrystallized by dissolving it in a minimum amount of warm water (*ca.* 50°) and filtering the solution warm. The solution was allowed to cool and filtered. More product was recovered by mixing the filtrate with a solution of 2 g. of sodium perchlorate monohydrate in about 3 ml. of water, allowing the solution to cool, and filtering it. The precipitates were washed with small volumes of ice water, 95% ethanol, and ether successively; total yield 0.7 g., 31%.

Anal. Calcd. for $C_{12}H_{22}O_8N_2CoCl$: C, 34.58; H, 5.28; N, 6.72. Found: C, 34.79; H, 5.25; N, 6.29.

Bis(acetylacetonato)2,2′-bipyridinecobalt(III) Iodide.—Recrystallized sodium dinitrobis(acetylacetonato)cobaltate(III) (2.0 g., 5.4 mmoles) was dissolved in 50 ml. of cold water and 20 ml. of methanol. Then 1.5 g. of Norit A carbon and 0.84 g. of 2,2′-bipyridine (5.4 mmoles) dissolved in 15 ml. of methanol were added simultaneously to the solution of the complex. The solution was stirred vigorously for 15 min. and then filtered by suction. The carbon was washed twice with 5-ml. portions of methanol, and the washings were combined with the red-brown filtrate. A solution of 1.0 g. of sodium iodide (6.7 mmoles) dissolved in 3 ml. of water was added to the above filtrate. The solution was stirred, allowed to cool, and filtered. The silvery red-brown crystals were washed with 5 ml. of ice water.

The product was recrystallized by dissolution in a minimum volume of boiling methanol and filtration while hot. The solution was allowed to cool and then refiltered. Then 5 to 10 ml. of ether was added to the methanol filtrate to recover further product. The precipitates were washed with small volumes of methanol and ether, consecutively; total yield of recrystallized product 0.7 g., 24%.

Anal. Calcd. for $C_{20}H_{22}O_4N_2CoI$: C, 44.46; H, 4.08; N, 5.19. Found: C, 44.46; H, 4.31; N, 5.04.

The crystalline form of the product varied with the method of precipitation. When the product was precipitated quickly by the addition of ether to methanol solutions of the complex, the product was a fine, amorphous precipitate; but when the complex was precipitated by slowly cooling the warm methanol solutions, the product was crystalline in character.

Bis(acetylacetonato)2,2′-bipyridinecobalt(III) Perchlorate.—The initial procedure for the formation of the complex in the presence of carbon and the filtration of the resulting solution were identical with the preparation of bis(acetylacetonato)2,2′-bipyridinecobalt(III) iodide. After the carbon had been removed by filtration, 1.0 g. of sodium perchlorate monohydrate (7.1 mmoles) dissolved in 3 ml. of water was added to the filtrate with stirring. The solution was allowed to cool and filtered. The precipitate was washed twice with 5-ml. portions of ice water.

The pink product was recrystallized by dissolution in about 160 ml. of boiling methanol and filtration while hot. The solution was allowed to cool and then filtered. The precipitate was washed with a small portion of methanol and ether; total yield of recrystallized product 0.66 g., 24%.

Mixed Bis(acetylacetonato)diamminecobalt(III) Iodides.—Recrystallized sodium dinitrobis(acetylacetonato)cobaltate(III) (2.0 g., 5.4 mmoles) was dissolved in 50 ml. of cold water. Then 1.0 g. of Norit A and 3 ml. of 6 *M* aqueous ammonia (18 mmoles) were added simultaneously and the solution was stirred vigorously for 10 min. at room temperature. The mixture was filtered by suction. The carbon was washed with two 5-ml. portions of water, and the washings were combined with the resultant solution. A solution of 10 g. of sodium iodide (66 mmoles) was added to the solution, which then was evaporated to one-half volume with a rotary evaporator at room temperature. The solution was filtered and the violet-brown precipitate was washed with two 5-ml. portions of ice water.

The product was recrystallized by dissolution in a minimum volume of warm water (*ca.* 50°) and filtration of the warm solution. Upon cooling, the violet-brown solid reprecipitated and was filtered. A solution of 2.0 g. (13 mmoles) of NaI dissolved in 2 ml. of water was added to the filtrate to obtain further product. The precipitates were washed with small volumes of ice water, 95% ethanol, and ether; total yield of recrystallized product 0.72 g., 32%.

Anal. Calcd. for $C_{10}H_{20}O_4N_2CoI$: C, 28.72; H, 4.79; N, 6.70; I, 30.37. Found: C, 28.77; H, 4.41; N, 6.90; I, 29.85.

trans-Bis(acetylacetonato)diamminecobalt(III) Iodide.—To 50 ml. of water heated to 75°, 1 g. of Norit A and 3 ml. of concentrated ammonium hydroxide (48 mmoles) were added with stirring. Then 2.0 g. of finely powdered, recrystallized sodium dinitrobis(acetylacetonato)cobaltate(III) (5.4 mmoles) was added with stirring. The solution was stirred for 10 min. at 75° and filtered by suction. The carbon was washed with two 5-ml. portions of hot water. A solution of 7.0 g. of sodium iodide (46 mmoles) in 10 ml. of water was added to the combined filtrate and washings.

The solution was evaporated to two-thirds volume and filtered. The resulting crystals were washed with a 5-ml. portion of ice water. This fraction (1) appeared to be richer in the violet *cis* crystals. The remaining solution was evaporated to about one-third of the original volume. The solution was filtered and the precipitate was washed with 5 ml. of ice water. This fraction (2) appeared to be richer in the bronze *trans* crystals.

The fraction 1 crystals were ground with 50 ml. of a 4:1 by volume ethanol–ether solution to remove the violet *cis* form. The solution was filtered, and the remaining crystals were treated with another 50 ml. of the ethanol–ether solution and filtered. The crystals left after the extraction were primarily the bronze *trans* form.

The violet crystals were extracted from fraction 2 in a similar manner using two 30-ml. portions of the ethanol–ether solution. Primarily the bronze form was left after extraction.

The bronze crystals left after the extractions of fractions 1 and 2 were combined, giving approximately 0.6 g. (1.45 mmoles) of the crude *trans*-$[Co(acac)_2(NH_3)_2]I$. This salt was dissolved in about 80 ml. of a solution of ethanol and water, 4:1 by volume, and the resulting solution was filtered. About 30 ml. of ether was added to the filtrate, resulting in the precipitation of the bronze complex. The solution was filtered and the precipitated product was washed twice with 5-ml. portions of an ethanol–ether

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(22) All analyses by Huffman Laboratories, Wheatridge, Colo.

solution, 4:1 by volume. N.m.r. spectra indicate that the bronze product is the pure *trans* isomer; yield 0.39 g., 17%.

cis-**Bis(acetylacetonato)diamminecobalt(III) Iodide.**—The filtrates from the extractions of fractions 1 and 2 in the preceding section containing primarily the *cis*-diammine isomer were combined and evaporated to dryness, giving about 0.75 g. of crude product.

The crude *cis* crystals were extracted again in the same manner as in the previous section using about 120 ml. of an ethanol–ether solution, 4:1 by volume. The solution was filtered and evaporated to dryness.

The crystals remaining after evaporation were extracted a third time. This time the crystals were extracted with about 50 ml. of an ethanol–water–ether solution, 4:1:1 by volume, and filtered. The filtrate was evaporated to about one-half volume and refiltered. The crystals recovered were washed with two 4-ml. portions of a cold ethanol–ether solution, 1:1 by volume. N.m.r. spectra showed this to be the pure *cis* product; yield 0.08 g., 3.4%.

Chloroform extractions of the *cis* isomer were used as an alternative procedure for the separation of the *cis* and *trans* isomers. The chloroform evaporated faster, a definite advantage.

trans-**Bis(acetylacetonato)diamminecobalt(III) Chloride.**—Silver chloride was made by dissolving 0.20 g. of silver nitrate (1.2 mmoles) in 10 ml. of water and adding an excess of concentrated sodium chloride solution. The silver chloride was filtered and washed with 10 ml. of water and 5 ml. of ethanol. Then 0.39 g. of *trans*-$[Co(acac)_2(NH_3)_2]I$ (0.93 mmole) was ground with the freshly precipitated silver chloride in 15–20 ml. of an ethanol–water solution, 4:1 by volume. After filtration the silver iodide was washed with two 5-ml. portions of the ethanol–water solution. The combined filtrates were evaporated to dryness. The bronze crystals were recrystallized by dissolution in about 15 ml. of warm ethanol (*ca.* 55°) and filtration of the warm solution. Then 15 ml. of ether was added to the filtrate and the mixture was allowed to cool. The solution was filtered and the precipitate was washed with two 5-ml. portions of an ethanol–ether solution, 1:1 by volume; yield 0.18 g., 60%.

cis-**Bis(acetylacetonato)diamminecobalt(III) Chloride.**—Silver nitrate (0.16 g., 0.96 mmole) was dissolved in 10 ml. of water. Silver chloride was precipitated by adding an excess of a concentrated aqueous sodium chloride solution. The solution was filtered, and the precipitated silver chloride was washed with 10 ml. of water and 5 ml. of ethanol.

The freshly precipitated silver chloride was ground thoroughly with 0.31 g. of *cis*-bis(acetylacetonato)diamminecobalt(III) iodide (0.71 mmole) in 15 ml. of ethanol. After filtration, the silver iodide was washed with two 5-ml. portions of ethanol. The combined filtrate and washings were evaporated to dryness.

The violet crystals were recrystallized by dissolving them in about 10–15 ml. of ethanol. The solution was allowed to evaporate to about one-half its volume. The solution was cooled and filtered. The crystals were washed with two 1-ml. portions of cold ethanol; yield 0.16 g., 66%.

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 of the complexes were obtained with a Cary Model 14 recording spectrophotometer or a Beckman Model DB recording spectrophotometer using aqueous or methanolic solutions in 1-cm. cells.

Proton N.m.r. Spectra.—All proton n.m.r. spectra were obtained on a Varian Model A-60 high-resolution spectrometer at 60 Mc. using tetramethylsilane as an internal standard whenever possible. The D_2O spectra are relative to a tetramethylsilane external standard (TMS–$CHCl_3$–CCl_4 solution, 1:5:5 by volume).

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N,N′-Dicyclohexylthiourea and N,N′-Diphenylthiourea Complexes of Cobalt(II)

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The N,N′-dicyclohexylthiourea (DCTU) and N,N′-diphenylthiourea (DPTU) complexes of Co(II) have been investigated. In organic solvents four-coordinated tetrahedral (or pseudo-tetrahedral) species are formed. Evidence is presented to indicate that both ligands undergo a structural change in solution (postulated to be a *cis–trans* isomerism) which affects their coordinating tendencies. The solid complexes $[Co(DCTU)_6]X_2$ (X = NO_3, ClO_4) involve octahedrally-coordinated Co(II), providing the first examples of six-coordinated Co(II) complexes containing solely unidentate sulfur ligands. The factors governing the coordination number of the complexes, both in solid state and in solution, are discussed.

Introduction

Cotton, *et al.*,[1] have recently reported the syntheses and physical properties of a series of compounds involving thiourea (TU) coordinated to the Co(II) ion. They found that the complexes are tetrahedral, except $Co(TU)_4(NO_3)_2$, which is probably octahedral. From the analyses of their electronic spectra, it was inferred that thiourea occupies a position comparable to various oxygen ligands in the spectrochemical series and that it

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[1] F. A. Cotton, O. D. Faut, and J. T. Mague, *Inorg. Chem.*, **3**, 17 (1964).