excessive steric crowding of the adjacent Co(acacen) moieties in III, rendering it a less plausible structure than I. One can arrive at a similar conclusion by the use of molecular models. Structure I most certainly represents a more polar molecule than does II and on this basis we tentatively assign I to the purple isomer isolated from the more polar methylene chloride solvent and II to the green isomer.

Structures I and II can account for a diamagnetic electronic configuration by enabling the TCNE to act as a "bridge," thereby providing a suitable molecular orbital for the unpaired electron on each cobalt(II) ion to become paired. This does not necessarily imply that in the solid state there is a complete transfer of electron density from the Co(acacen)py moiety to the TCNE ligand. The mull ir spectrum of the green or purple isomer does not agree with the published spectrum of $TCNE^-$ [3a,11] or $TCNE^{2-}$ [11] (see Table I). However, apparently complete electron transfer does occur in methylene chloride solution as the electronic solution spectrum of both isomers indicates the presence of $TCNE^-$ in this solvent (see Figure 2 and Results).

Coordination through the nitrogen atoms as shown in I above should give rise to an ir-active C=C stretching frequency.[11] However, due to strong absorptions in this region by the Schiff base ligand, positive identification of such a band is not possible.

Nitrogen coordination as described above provides a reasonable mechanism by which a polymeric species involving a continuous chain of alternating TCNE–Co(acacen) groups could be formed. Such is a possible structure for the intractable solid isolated from benzene or toluene solutions in the absence of pyridine. Elemental analysis gives $[Co(acacen)TCNE]_n$ as the approximate stoichiometry and ir absorptions in the C≡N stretching region are similar to those observed for the well-behaved green and purple isomers (see Table I).

In conclusion, our results support formulating the purple and green complexes of composition $[Co(acacen)py]_2TCNE$ as geometric isomers having I and II, respectively, as their most probable structures.

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CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
CARNEGIE-MELLON UNIVERSITY, PITTSBURGH, PENNSYLVANIA 15213

Stereochemistry of β-Diketone Complexes of Cobalt(III). VI. Synthesis and Spectroscopy of *cis*- and *trans*-Nitroaminebis(acetylacetonato)cobalt(III)

BY L. J. BOUCHER* AND N. G. PAEZ

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cis- and *trans*-nitroaminebis(acetylacetonato)cobalt(III) complexes, where amine is ammonia, methylamine, dimethylamine, trimethylamine, piperidine, and aniline, have been synthesized and characterized. The stereochemistry of the complexes can be assigned with the aid of their proton magnetic resonance spectra. In addition, infrared and ultraviolet–visible spectra of the materials were determined and the absorption bands assigned. In chloroform solution all the trans complexes isomerize to form only the cis isomers, with the rate of conversion dependent on the amine. The aniline complex isomerizes several orders of magnitude faster than the other complexes and also shows a slow conversion in the solid state.

The synthesis and characterization of a large number of amine complexes of the type *trans*-$Co(acac)_2NO_2L$[1] have been reported.[2] Although many heterocyclic amine derivatives are known,[3] no alkylamine complexes have been previously characterized. A brief report of the trans → cis isomerization of the pyridine complex and the isolation of the only previously known cis isomer of this type has appeared.[4] To determine the effect of the donor strength of the amine on the isomerization and ligand-exchange reactions of the $Co(acac)_2NO_2L$ complexes, we have first prepared and characterized the cis,trans isomer pairs for a number of alkylamines. The complexes reported here are listed in Table I and a structural representation is shown in Figure 1.

(1) acac = 2,4-pentanedionato (acetylacetonato).
(2) L. J. Boucher and J. C. Bailar, Jr., *J. Inorg. Nucl. Chem.*, **27**, 1093 (1965).
(3) C. Varnelyi and A. Kezsmarky, *Stud. Univ. Babes-Bolyai, Ser. Chem.*, **14**, 79 (1969).
(4) L. J. Boucher and N. G. Paez, *Inorg. Chem.*, **9**, 418 (1970).

Experimental Section

Materials.—The starting material, $Na[trans\text{-}Co(acac)_2(NO_2)_2]$, was prepared as previously described.[2] The amines used were reagent grade (Eastman Organic Chemicals) and used without further purification.

Synthesis. *trans*-$Co(acac)_2NO_2L$.—Four grams (1.1×10^{-2} mol) of $Na[Co(acac)_2(NO_2)_2]$ were dissolved in 100 ml of distilled water and 2 g of the liquid amine ligand (>2-fold excess) added. Aqueous solutions of methylamine (40%), trimethylamine (25%), dimethylamine (25%), and ammonia (25%) were used. The resulting mixture was stirred at room temperature for 10 min (4 hr for ammonia) and then filtered. In the case of the ammonia and aniline reactions, the desired product precipitated out of solution. The red-brown powder was collected on a funnel and washed with 50 ml of distilled water and air dried (yield ~75%). In the case of the other amines the desired product remained in solution. The aqueous reaction mixture was extracted with 100 ml of chloroform (four times). The deeply colored chloroform layer was separated and evaporated to dryness. The residue was taken up in a small amount of chloroform and the product was precipitated by the addition of petroleum ether (bp 30–60°). The red-brown powder was collected and air dried (yield ~40%).

cis-$Co(acac)_2NO_2L$.—One gram of the corresponding trans isomer was dissolved in 75 ml of chloroform and the resulting

TABLE I
ELEMENTAL ANALYSES OF $Co(acac)_2NO_2L$

L	Isomer	Mp, °C	% C Calcd	% C Found[a]	% H Calcd	% H Found	% N Calcd	% N Found
NH_3	Trans	170	37.50	37.42	5.31	5.44	8.75	8.61
	Cis	169		37.68		5.40		8.57
NH_2CH_3	Trans	139	38.48[b]	38.36	5.88	5.72	8.16	7.88
	Cis	155	39.53	39.47	5.73	5.83	8.38	8.32
$NH(CH_3)_2$	Trans	150	41.39	41.15	6.08	5.95	8.04	7.93
	Cis	154		41.22		6.07		7.93
$N(CH_3)_3$	Trans	133	43.10	43.32	6.40	6.37	7.73	7.62
$NH_2C_6H_5$	Trans	140	48.49	48.20	5.34	5.19	7.07	7.15
	Cis	148		48.37		5.17		7.31
NHC_5H_{10}	Trans	134	46.40	46.29	6.49	6.22	7.21	7.06
	Cis	155		46.06		6.51		7.26

[a] Performed by Galbraith Laboratories, Inc., Knoxville, Tenn. [b] For 0.5 water of crystallization; average of duplicate analysis.

solution was refluxed for 3 hr. The cooled chloroform solution was filtered and the filtrate evaporated to dryness. The residue was recrystallized from chloroform–petroleum ether and air dried (yield ~85%).

Spectroscopy.—Nuclear magnetic resonance spectra were obtained with a Hitachi Perkin-Elmer R-20 high-resolution spectrometer at 60 MHZ, at 34°. Chemical shifts, to ±0.01 ppm, were measured relative to an internal standard with a frequency counter. Samples were dissolved to 5% (w/v) in the appropriate deuterated solvents (obtained from Diaprep, Inc.) and the internal standards used were chloroform–tetramethylsilane, dimethyl sulfoxide–hexamethyldisiloxane, and water–3-trimethylsilyl-1-propanesulfonate. Ultraviolet and visible absorption spectra were obtained with a Cary 14 recording spectrophotometer. Infrared spectra were obtained with a Perkin-Elmer Model 237 spectrophotometer in the 4000–400-cm^{-1} range with the materials in potassium bromide disks.

Results and Discussion

Synthesis.—The synthetic scheme utilized in this work can be summarized as

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

$$trans\text{-}Co(acac)_2(NO_2)H_2O + L \rightleftharpoons trans\text{-}Co(acac)_2(NO_2)L + H_2O \quad (2)$$

$$trans\text{-}Co(acac)_2NO_2L \rightleftharpoons cis\text{-}Co(acac)_2NO_2L \quad (3)$$

Reaction 1 is very rapid with the equilibrium being established in a few minutes at 25°.[5] When excess amine is added, reaction 2 also takes place rapidly with the equilibrium strongly shifted in favor of the amine complex. The general rapidity of reactions 1 and 2 can be attributed to the trans effect of the NO_2^- in these complexes. For aniline and ammonia the trans complex is not greatly soluble in water and the product precipitates out of solution (yield ~75%). As the filtrate is still colored, some of the amine complexes probably remain in the aqueous solution. For pyridine, where the products are highly insoluble in water, the yield for reaction 2 approaches the quantitative limit.[2] In the ammonia preparation the ammonium salt of *trans*-$Co(acac)_2(NO_2)_2^-$ initially precipitates out of solution with the desired product. Aging the precipitate in the presence of the mother liquor for several hours gives a conversion of the ammonium salt into the ammonia complex. In contrast to other amines, the alkylamine complexes are soluble in water and reaction 2 does not lead to the precipitation of the desired product. In this case the product must be extracted out of the aqueous phase into chloroform. After several extractions, a reasonable yield of product can be obtained (~40%). The colored aqueous phase probably still contains some amine complex as well as hydrolysis products.

(5) B. P. Cotsoradis and R. D. Archer, *Inorg. Chem.*, **6**, 800 (1967).

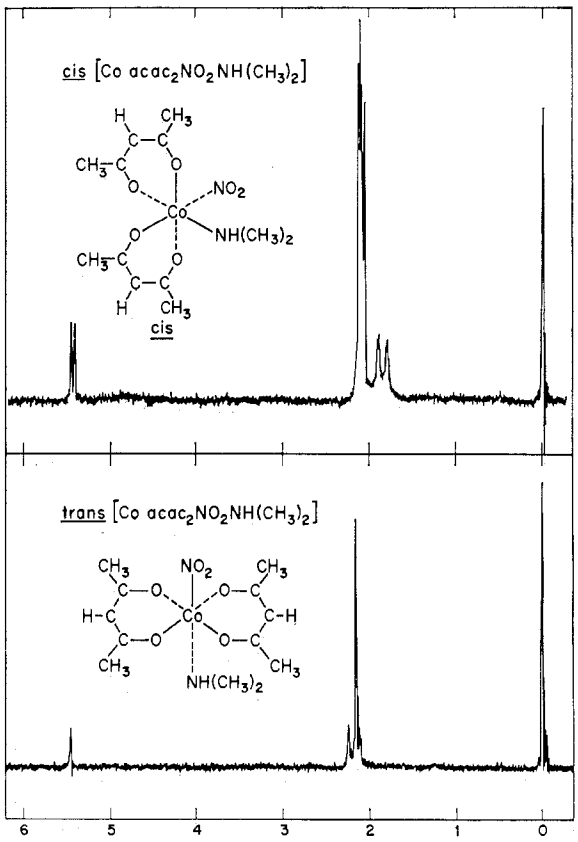

Figure 1.—Proton magnetic resonance spectra of nitrodimethylaminebis(acetylacetonato)cobalt(III) in deuteriochloroform.

The materials isolated from aqueous solution *via* the precipitation or extraction are isomerically pure. The isomerization reaction (eq 3) proceeds smoothly in boiling chloroform with essentially complete conversion to the cis isomer. No by-products or decomposition products are generally observed. Therefore, the synthetic procedure gives the pure trans and cis isomers, and there is no need for tedious separation of mixtures of the isomers. The only exception to this scheme is provided by the trimethylamine reaction. Surprisingly, the isomerization reaction in refluxing chloroform yields a number of products, including *cis*- and *trans*-$Co(acac)_2(NO_2)_2^-$, $Co(acac)_3$, *cis*- and *trans*-$Co(acac)_2NO_2N(CH_3)_3$, as well as other unidentified products. The yield of the cis isomer, about 10%, is the same as that of the trans isomer. Although it takes somewhat longer, room-temperature isomerization in chloroform yields the same distribution of products. A small amount of cis isomers can be isolated with the aid of preparative thin layer chromatography plates.[4] However, not enough material was isolated to obtain elemental analyses.

The trans isomers are red-brown while the cis isomers are red-purple solids. Elemental analyses of the recrystallized materials are given in Table I. Except for the trimethylamine derivative, the complexes are stable at room temperature in chloroform, dimethyl sulfoxide (DMSO), methanol, and water for several hours. After several days the complexes, in the latter two solvents, show extensive decomposition. For chloroform and dimethyl sulfoxide solutions, no decomposition is

noted during a comparable period. Extended heating (~60°), however, of the dimethyl sulfoxide solution does eventually lead to decomposition of the complexes. In good coordinating solvents like water, methanol, and dimethyl sulfoxide, some amine displacement by the solvent is expected for the trans isomers.[5] Rapid ligand-exchange reactions for complexes of this type have been noted previously[4] and ascribed to an octahedral trans effect of the nitro ligand: *trans*-$Co(acac)_2NO_2L + S \rightleftarrows$ *trans*-$Co(acac)_2NO_2S + L$. In water it appears that the ratio of the NH_2CH_3 complex to the aquo complex is about 7:1 while in DMSO there appears to be little solvent complex formed. No solvolysis in DMSO is noted for the NH_3, NH_2CH_3, $NH(CH_3)_2$, and $NH(C_5H_{10})$ complexes. Conversely, the $NH_2C_6H_5$ and $N(CH_3)_3$ complexes show amine:DMSO complex ratios of 1:1 and 1:4. It appears that DMSO can compete with the amine only in those cases where the amine donor is weak. None of the cis isomers initially shows solvolysis in good coordinating solvents. However, for the aniline complex there is slow cis to trans isomerization and then the trans isomer solvolyzes. For example, the equilibrium of the mixture of the aniline complex in DMSO, starting with either the cis or trans isomer, shows the ratio of cis (aniline) to trans (aniline) to trans (DMSO) of 2:1:1. The equilibrium is established in a few days at room temperature. Aqueous and methanol solutions of both the cis and trans isomers slowly decompose at room temperature after a few days. This probably occurs *via* an initial solvolysis of the trans amine complex with a subsequent loss of the nitro ligand. This scheme would also require a cis to trans isomerization for the cis isomer. The solvent complex then undergoes irreversible redox decomposition to a cobalt(II) salt. This pathway has been substantiated for the aqueous solvolysis of *trans*-$Co(acac)_2(NO_2)_2^-$.[6]

The isomerization reaction of the trans complexes appears to proceed smoothly in chloroform. The equilibrium strongly favors the cis isomer at 60° (as well as 45 and 25°). Since it would be difficult to detect less than 5% trans in a mixture of isomers, an estimate of the equilibrium constant for these isomerizations would be $K > 20$. This result is contrasted with the pyridine complex which shows nearly equal amounts of the cis and trans isomers at equilibrium at 60°.[4] If there were no thermodynamic difference (bond strength) between the cis and trans isomers, the equilibrium constant for trans to cis would be 4 (statistical distribution). The fact that the cis isomer is favored for the alkylamine complexes can be easily rationalized by taking into account the proposed nitro trans effect. In the trans isomer the strong donor NO_2^- is competing for the metal σ orbital (p_z) with a strong donor amine. On the other hand, in the cis isomer both strong nitrogen donors are competing for the σ orbitals with the weak donor oxygen atoms of the acetylacetone ligand. As a result the nitrogen donors form stronger bonds in the cis isomers than in the trans and therefore the cis isomer is thermodynamically favored. The question still remains as to why the pyridine complex should show a depressed stability of the cis isomer. A simple rationalization of this anomaly may be related to intramolecular hydrogen-bonding effects. Interaction of the cis nitro and alkylamine ligands might stabilize these cis isomers enough to lead to the observed results.

The rate at which the trans isomer isomerizes to the cis isomer is a function of the amine. The $t_{1/2}$ order for the reaction at 49° in $CHCl_3$ is $NH(C_5H_{10}) > NH(CH_3)_2 > NH_2CH_3 >> NH_2C_6H_5$; *i.e.*, aniline isomerizes the fastest while the piperidine isomerizes the slowest. The pyridine derivative appears near piperidine in the order. Surprisingly, the aniline derivative isomerizes very rapidly ($t_{1/2} \sim 0.1$ hr at 25°), *i.e.*, about 10^3 times faster than the piperidine complex. The facile trans to cis isomerization of the aniline complex has also been observed for the solid. Dry heating of the complex, *in vacuo*, at 105° for several hours gives rise to isomerization as well as extensive decomposition. Conversely, heating at 80° for 48 hr yielded isomerization to a predominantly cis product with no evidence of decomposition.

Spectroscopy.—The visible–ultraviolet absorption spectra, infrared spectra, and nuclear magnetic resonance spectra of the various materials were determined. Although all of them are needed for characterization, only the proton magnetic resonance spectra are useful in assigning stereochemistry.[7] It is readily seen that in the trans isomer, all the acetylacetonate methyl and methine groups are related to each other by symmetry elements of the molecule and are therefore equivalent.[8] The pmr spectra of the trans isomers should then show one methyl and one methine resonance in the intensity ratio 6:1. Figure 1 shows a typical spectrum of a trans isomer. For the cis isomer neither the methyl groups nor the methine protons are related to each other by any symmetry element of the molecule. Since all four methyl groups and the two methine protons are nonequivalent, four methyl resonances and two methine resonances in the ratios 3:3:3:3:1:1 are expected in the pmr spectrum. This is nicely borne out by the spectrum of a typical cis isomer shown in Figure 1. In some cases, however, only three of the methyl resonances, in the ratio 6:3:3, are resolved while the methine resonances also can overlap each other to give a single broad line. The stereochemistry of all the complexes reported here has been assigned using the nmr method. Further, the relative amounts of the isomers in mixtures and of the solvolysis products can be roughly estimated by considering the intensity of the various proton resonances.

The nmr spectral data for the complexes in a number of solvents are summarized in Table II and a typical spectrum is shown in Figure 1. The spectrum of the ammonia complex could not be determined in $DCCl_3$ because of insufficient solubility. In addition to the resonances which arise from the methyl and methine protons of the acetylacetonate ligand, the alkyl and aryl protons of the amine are also seen. The positions of these resonances are listed in Table II under the last column. The expected triplet and doublet patterns for the methyl resonances of the methylamine and dimethylamine, which arise from spin–spin coupling ($J \approx 6$ Hz) with two and one amine protons, are observed. Only a broad band for the methylene proton of the piperidine

(6) R. J. Kline and R. A. Velapoldi, *Inorg. Chem.*, **9**, 1312 (1970).

(7) R. C. Fay and T. S. Piper, *J. Amer. Chem. Soc.*, **84**, 2303 (1962).

(8) L. J. Boucher, E. J. Battis, and N. G. Paez, *J. Inorg. Nucl. Chem.*, in press.

TABLE II
PROTON MAGNETIC RESONANCE DATA (PPM) FOR $Co(acac)_2NO_2L$

L	Isomer	Solvent	Resonance CH_3	Resonance C–H	Resonance L
NH_3	Trans	DMSO	−1.95	−5.43	
NH_3	Cis	DMSO	−1.97	−5.44	
			−1.93		
			−1.92		
NH_3	Cis	$DCCl_3$	−2.16	−5.48	
			−2.11		
			−2.06		
NH_2CH_3	Trans	D_2O	−2.17	−5.70	−1.87
NH_2CH_3	Trans	DMSO	−1.96	−5.46	−1.82
					−1.72
					−1.62
NH_2CH_3	Trans	$DCCl_3$	−2.15	−5.50	−2.32
					(−2.22)
					−2.11
NH_2CH_3	Cis	DMSO	−1.96	−5.45	−1.73
			−1.94		−1.63
			−1.92		−1.51
NH_2CH_3	Cis	$DCCl_3$	−2.16	−5.48	−1.93
			−2.12		−1.82
			−2.09		
			−2.05		
$NH(CH_3)_2$	Trans	DMSO	−1.97	−5.50	−1.88
					−1.78
$NH(CH_3)_2$	Trans	$DCCl_3$	−2.17	−5.50	−2.26
					(−2.16)
$NH(CH_3)_2$	Cis	DMSO	−1.97	−5.48	−1.78
			−1.95	−5.45	−1.68
			−1.92		
$NH(CH_3)_2$	Cis	$DCCl_3$	−2.12	−5.48	−1.90
			−2.11	−5.43	−1.80
			−2.08		
			−2.05		
$N(CH_3)_3$	Trans	DMSO	−2.00	−5.48	−2.14
$N(CH_3)_3$	Trans	$DCCl_3$	−2.17	−5.48	−2.10
$N(CH_3)_3$	Trans	$C_6D_5NO_2$	−1.94	−5.44	−2.08
$N(CH_3)_3$	Cis	$DCCl_3$	−2.20	−5.52	−2.07
			−2.07	−5.47	
			−1.98		
$NH_2C_6H_5$	Trans	DMSO	−1.86	−5.31	
$NH_2C_6H_5$	Trans	$DCCl_3$	−2.09	−5.39	
$NH_2C_6H_5$	Cis	DMSO	−1.94	−5.39	
			−1.87	−5.09	
			−1.72		
			−1.66		
$NH_2C_6H_5$	Cis	$DCCl_3$	−2.12	−5.46	
			−1.90	−5.04	
			−1.86		
NHC_5H_{10}	Trans	DMSO	−1.97	−5.48	−1.48
NHC_5H_{10}	Trans	$DCCl_3$	−2.15	−5.48	−1.69
NHC_5H_{10}	Cis	DMSO	−1.98	−5.49	−1.52
			−1.94	−5.43	
			−1.92		
NHC_5H_{10}	Cis	$DCCl_3$	−2.12	−5.45	−1.69
			−2.10	−5.42	
			−2.08		
			−2.06		

complex is seen, however. The phenyl proton multiplets of the aniline complex are seen in the downfield region around −7.0 ppm. Because of limited solubility in chloroform and nitrogen quadrupole broadening, the amine proton resonances of the complexes could only be determined for the methylamine complex. The cis and trans isomers each show a single broad resonance at −3.80 and −3.16 ppm, respectively.

The chemical shifts of the acetylacetonate methyl and methine protons vary only slightly with the amine. For example, for the trans complexes average values of the chemical shifts are −1.97 ± 0.02 and −5.46 ± 0.03 ppm in DMSO and −2.16 ± 0.01 and −5.49 ± 0.01 ppm in $CDCl_3$. The aniline complex does not fall within these ranges with the proton resonances shifted 0.08–0.15 ppm upfield. This is undoubtedly a consequence of the magnetic anisotropy of the phenyl substituent.[8] The cis isomers show average values for the methyl and methine resonances of −2.10 ± 0.01 and −5.46 ± 0.02 ppm for $CDCl_3$ and −1.94 ± 0.01 and −5.45 ± 0.01 ppm for DMSO solutions. Again the aniline derivatives show resonances shifted upfield by 0.11–0.21 ppm. Within experimental error there appears to be no correlation of base strength of the amine and the proton resonance of the acetylacetonate anion for both isomers; *i.e.*, there is no evidence for a ground-state cis or trans effect.[9] The splitting of the nonequivalent methyl and methine protons in the cis isomer does appear to be slightly dependent on the amine. The largest splitting by far is for the nonequivalent methine proton resonances of the aniline complex; *e.g.*, it is 0.42 ppm for $CDCl_3$ solutions. For the methyl resonances aniline also shows the greatest splitting, 0.28 ppm. The large splitting with this amine can be associated with the magnetic anisotropy of the phenyl ring. The large splitting of the nonequivalent methyl resonances for the trimethylamine complex may be related to the bulky nature of the ligand. Solvation effects are probably important here.[10] In fact, it is observed that an increase of alkyl groups in the ligands, which would change the solvation pattern, increases the splitting.

Comparison of the individual complexes for $CDCl_3$ and DMSO solutions show that there are only small upfield shifts less than 0.10 ppm in going from the trans to the cis isomers. The magnitude of the shift is dependent on the amine. The observed upfield shift is in direct contradiction to the predicted downfield shift based on the electric field model; *i.e.*, the increase in molecular dipole moment in going from the trans to the cis isomer should lead to an appreciable downfield shift.[11] Some previous work indicates that acetylacetonate proton resonances are not sensitive to electric field effects.[12] This also appears to be the case with the methyl protons on the amine ligands since upfield shifts of ~0.10 ppm in DMSO and ~0.35 ppm in $CDCl_3$ are noted in going from the trans to the cis isomer. All the upfield shifts may be related to solvation effects. It is interesting to note that the amine proton resonances show a substantial downfield shift, 0.64 ppm, in going from the trans to the cis isomer. This downfield shift may be a consequence of a relatively large electric field effect which arises because the protons are close to the metal. An alternate rationalization is that the amine protons are shielded in the trans isomer because of the trans effect of the nitro groups.[9] Hydrogen bonding of the amine proton to the nitro groups in the cis isomer might also lead to a downfield shift. A study of the pmr spectra of the halopentaammine-cobalt(III) complexes has also shown that the amine protons cis to the X group are substantially downfield from the trans amine protons.[13]

The infrared spectra, 4000~400 cm^{-1}, were deter-

(9) H. A. O. Hill, K. G. Morallee, and G. Pellizer, *J. Chem. Soc. A*, 2096 (1969).
(10) R. J. York, W. D. Bonds, B. P. Cotsoradis, and R. D. Archer, *Inorg. Chem.*, **8**, 789 (1969).
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(12) T. J. Pinnavia, L. J. Matienza, and Y. A. Peters, *Inorg. Chem.*, **9**, 993 (1970).
(13) D. N. Hendrickson and W. L. Jolly, *ibid.*, **9**, 1197 (1970).

TABLE III
ELECTRONIC ABSORPTION SPECTRA OF $Co(acac)_2NO_2L$

L	Isomer	$^1A_{1g} \rightarrow {}^1T_{1g}$ $\bar{\nu}$	ϵ	$t_{2g} \rightarrow \pi^*$ $\bar{\nu}$	ϵ	$\sigma L \rightarrow e_g$ $\bar{\nu}$	ϵ	$\pi \rightarrow \pi^*$ $\bar{\nu}$	ϵ
				CH_3OH Solvent					
NH_3	Trans	18.7	117	29.9	6,380	38.1	23,300	43.6	26,700
	Cis	18.6	164	30.9	7,400	39.2	29,400	44.8	25,800
NH_2CH_3	Trans	18.8	124	29.7	7,340	38.1	25,000	43.6	30,800
	Cis	18.6	157	30.9	6,920	39.1	29,800	44.4	27,600
$NH(CH_3)_2$	Trans	18.6	139	29.7	7,160	37.6	25,500	43.4	29,600
	Cis	18.3	153	30.8	6,740	38.9	32,000	44.0	29,000
$N(CH_3)_3$	Trans	17.8	131	29.8	5,700	37.3	21,800	43.3	23,200
$NH(C_5H_{10})$	Trans	18.6	148	29.7	7,080	38.1	24,800	43.3	27,100
	Cis	18.3	162	31.0	6,600	39.0	35,300	~44.0	...
$NH_2C_6H_5$	Trans	18.4	159	29.8	5,940	37.6	23,100	43.3	31,300
	Cis	18.1	203	32.5	14,900	38.2	27,300	44.2	23,200
				$CHCl_3$ Solvent					
NH_3	Trans	*a*							
	Cis	18.5	176	30.8	7,600	38.7	27,400	*b*	
NH_2CH_3	Trans	18.8	124	29.7	6,400	37.5	24,700		
	Cis	18.5	178	30.7	7,400	38.7	30,700		
$NH(CH_3)_2$	Trans	18.4	166	29.6	6,960	37.2	21,700		
	Cis	18.3	165	30.6	6,320	38.2	26,300		
$N(CH_3)_3$	Trans	17.8	179	30.7	6,000	37.3	23,800		
$NH_2(C_6H_5)$	Trans	18.4	196	~31.8	...	37.7	24,900		
	Cis	17.9	223	~32.0	...	37.6	24,600		
$NH(C_6H_{10})$	Trans	18.5	177	29.5	7,700	37.1	24,500		
	Cis	18.4	172	30.2	4,180	37.9	17,500		

[a] Insoluble. [b] Solvent absorption.

mined with the complexes in potassium bromide disks. The higher frequency region, >700 cm^{-1}, shows absorptions typical of the coordinated acetylacetonate anion, the N-bonded ligand, and the alkylamine.[14] The amine ligands show the following medium-intensity absorptions: ν(N–H) at 3310, 3250 cm^{-1} for NH_3, 3300, 3255 cm^{-1} for NH_2CH_3, 3220 cm^{-1} for $NH(CH_3)_3$, 3200 cm^{-1} for NHC_5H_{10}. Surprisingly, the aniline complexes are distinguishable; *i.e.*, the trans isomer shows ν(N–H) at 3320 and 3250 cm^{-1} while the cis isomer shows broad absorptions at 3230 and 3120 cm^{-1}. An intramolecular hydrogen bond between the nitrite oxygen and aniline NH_2 group in the cis isomer would be consistent with the broadening and lowering in frequency of the N–H stretches. It is interesting to note that there is no evidence for intramolecular hydrogen bonding of the amine to the acetylacetonate oxygen[15] since the other cis,trans isomer pairs show the same N–H frequencies. The low-frequency region of the spectra, 700–400 cm^{-1}, shows differences among the individual isomer pairs. Acetylacetonate ring deformation absorptions appear at 695, 670, and 635 cm^{-1}.[16] The latter band is clearly seen only for the cis isomers. The NO_2^- rock is seen at 600 cm^{-1} for both isomers. While the ν(Co–N) absorption should appear below 400 cm^{-1}, the ν(Co–O) absorptions are expected around 400–600 cm^{-1}. The cis isomers generally show a medium-intensity band in the 460–480-cm^{-1} region which can be assigned to the predominant mode, ν(Co–O) + δ(C–CH_3).[16] In addition a weak band is seen at 500–510 cm^{-1} which may arise from a chelate ring deformation. Conversely the trans isomer shows two medium-intensity absorptions at 440–460 and 480–500 cm^{-1}. The absorptions probably arise from predominant modes involving the cobalt–oxygen stretching and chelate ring or C–CH_3 deformations. Although symmetry considerations would predict otherwise, the trans isomer spectra show more absorptions than those of the cis isomers. Since the infrared absorptions arise from rather complicated motions involving the cobalt–ligand and ligand vibrations in these low-symmetry complexes, it is not useful to discuss the low-frequency spectra in terms of variation of the ligand or isomer.

Electron absorption spectra were determined with the complexes in methanol and chloroform. Typical spectra are shown in Figure 2 and the absorption maxima are listed in Table III. The visible spectra show one prominent absorption at 17.8–18.8 kK as well as a shoulder at ~27 kK. These absorptions can be assigned to the ligand field transitions $^1A_{1g} \rightarrow {}^1T_{1g}$ and $^1A_{1g} \rightarrow {}^1T_{2g}$ of the pseudooctahedral cobalt(III). Even though the low symmetry of the complexes gives rise to splitting of the octahedral levels and requires three components at each band, only broad unresolved absorp-

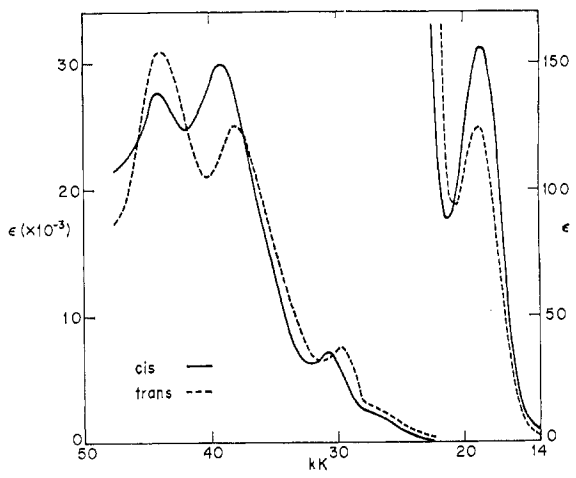

Figure 2.—Absorption spectra of nitromethylaminebis(acetylacetonato)cobalt(III) in methanol.

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tions are observed.[17] Nonetheless, the predicted increase in absorption intensity in going from the trans to the cis isomer is generally observed. The frequency of the ligand field maxima does vary ($\Delta < 1000$ cm^{-1}) with the amine: $NH_3 \sim NH_2CH_3 > NHC_5H_{10} \geq NH(CH_3)_2 > NH_2C_6H_5 > N(CH_3)_3$. The absorption is generally higher in energy ($\sim$200 cm^{-1}) for the trans as compared to the cis and higher ($\sim$100 cm^{-1}) in methanol than in chloroform. Previous work places the pyridine complex near methylamine in the ligand order.[4] The ligand order does not correspond to the proton basicity of the amine except for the fact that the weakest donor, aniline, appears to the lower end of the list. The order does, however, appear to be related to the bulkiness of the ligand.[18] Steric interactions prevent the formation of a strong bond with the cobalt atom and as a result the ligand field is weakened.

The ultraviolet spectra of the complexes show a relatively weak band at 29.6–32.5 and two strong absorptions at 37.1–39.2 and 43.0–45.0 kK. All the maxima are at higher energy for the methanol solutions than for the chloroform solutions. The low-energy, low-intensity absorption has been assigned to a metal to ligand, $t_{2g} \rightarrow \pi^*$, charge transfer on the basis of MO calculations.[19] The frequency of the maximum is independent of the amine. For example, in methanol solution the band position of the cis isomer is 31.0 ± 0.1 kK and of the *trans* isomer is 29.8 ± 0.1 kK. The only exception to this generalization is seen with aniline when the aromatic absorption shifts the apparent maximum to higher energy. Since the $t_{2g} \rightarrow \pi^*$ transitions only involve the π-bonding d orbitals, changing of the amine σ donor should not affect the energy of the transition. The next highest energy band in the uv spectrum has been variously assigned as a charge-transfer band or ligand band.[19] Recent work[20] indicates that a ligand to metal charge transfer, $\sigma_L \rightarrow e_g$, band should appear in this region for metal β-diketonates. This seems a reasonable assignment for cobalt(III) complexes. The absorption maximum appears to be dependent on the amine ($\Delta < 800$ cm^{-1}) in the same way as the ligand field band. This is to be expected since the energy of the e_g orbital of metal is dependent on the σ-donating ability of the amine. The high-energy band in the spectra has been assigned to $\pi \rightarrow \pi^*$ transition of the acetylacetonate anion.[19] As expected, the absorption maximum is independent of the amine ligand; *e.g.*, the maximum is at 43.4 ± 0.2 kK for the trans isomer and at 44.4 ± 0.4 kK for the cis isomer. There appears to be a substantial blue shift, $\sim$1000 cm^{-1}, of all the ultraviolet bands in going from the trans to the cis isomer. This effect is independent of the nitro ligand since it is observed for the diamine complex.[21]

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SOUTH AFRICAN COUNCIL FOR SCIENTIFIC AND INDUSTRIAL RESEARCH, PRETORIA, REPUBLIC OF SOUTH AFRICA

Cationic Complexes of Rhodium(I) and Their Reactivity toward Air[1]

BY LINDA M. HAINES

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The reaction of $[C_8H_{12}RhCl]_2$ with an excess of the ligands L = $P(O\text{-}i\text{-}C_3H_7)_3$, $P(OCH_3)_2C_6H_5$, $POCH_3(C_6H_5)_2$, $P(CH_3)_2C_6H_5$, and $PCH_3(C_6H_5)_2$ in methanol at room temperature or under refluxing conditions gives the four-coordinate cations RhL_4^+ whereas the corresponding reaction involving the ligands L = $P(OR)_3$ (R = CH_3, C_2H_5, $i\text{-}C_4H_9$, and $n\text{-}C_4H_9$) and $P(OCH_2)_3CCH_3$ yields the five-coordinate species RhL_5^+. However, by employing a rhodium:ligand ratio of 1:4 in those reactions involving the ligands $P(OR)_3$ (R = CH_3 and C_2H_5) the four-coordinate cations $Rh[P(OR)_3]_4^+$ are obtained. Further the reaction of $[C_8H_{12}RhCl]_2$ with excess of the ligands L = $P(CH_3)_2C_6H_5$ and $As(CH_3)_2C_6H_5$ in methanol in the presence of air affords the stable oxygen-containing cations $RhL_4O_2^+$. The cations RhL_4^+, RhL_5^+, and $RhL_4O_2^+$ were characterized as the tetraphenylborates, hexafluorophosphates, or perchlorates. The ionic compounds $\{Rh[P(OR)_3]_4\}B(C_6H_5)_4$ (R = CH_3, C_2H_5, and $i\text{-}C_3H_7$) and $\{Rh[P(OR)_3]_5\}B(C_6H_5)_4$ (R = CH_3, C_2H_5, $i\text{-}C_4H_9$, and $n\text{-}C_4H_9$) decompose in air to form the neutral derivatives $Rh[P(OR)_3]_2B(C_6H_5)_4$ containing one of the phenyl rings of the $B(C_6H_5)_4$ group bonded as an arene to the rhodium atom. The bonded $B(C_6H_5)_4$ group in $Rh[P(OCH_3)_3]_2B(C_6H_5)_4$ is readily displaced by trimethyl phosphite and by the ligand $(C_6H_5)_2PC_2H_4P(C_6H_5)_2$ to give the products $\{Rh[P(OCH_3)_3]_5\}B(C_6H_5)_4$ and $\{Rh[(C_6H_5)_2PC_2H_4P(C_6H_5)_2]_2\}B(C_6H_5)_4$, respectively. The compound $\{Rh[P(OCH_3)_3]_5\}PF_6$ reacts with the dienes cycloocta-1,5-diene and bicyclo[2.2.1]hepta-2,5-diene in the presence of air to give the ionic derivatives $\{Rh(C_8H_{12})[P(OCH_3)_3]_2\}PF_6$ and $\{Rh(C_7H_8)[P(OCH_3)_3]_3\}PF_6$, respectively. The nmr spectra of the various compounds are discussed.

Introduction

The chemistry of neutral phosphine derivatives of rhodium(I) has received considerable attention of late, particularly since the discovery that $Rh[P(C_6H_5)_3]_3Cl$[2] and $RhH(CO)[P(C_6H_5)_3]_3$[3,4] are effective homogeneous catalysts for the hydrogenation and hydroformylation

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