complex has an (*R*)-asymmetric nitrogen at the end of chelate ring. The vicinal effect from this (*R*)-asymmetric nitrogen has been obtained from the circular dichroism spectra of *trans*-Co(LL-1,3,8,10-Me_4trien)Cl_2^+ and *trans*-Co(LL-3,8-Me_2trien)Cl_2^+ and is represented in Figure 6 with that[29] from (−)D-*trans*-Co(N-Meen)Cl_2^+ and *trans*-Co(*d*-pn)$_2Cl_2^+$. These two vicinal effects are very similar and have a positive Cotton effect for the $A_{1g} \rightarrow E_g(D_{4h})$ component and a negative Cotton effect for the $^1A_1 \rightarrow {}^1A_2$ component. This result indicates that the vicinal effect from (*R*)-asymmetric nitrogen does not depend on the positions of the two (*R*)-asymmetric nitrogen (*i.e.*, *trans* for *trans*-Co(N-Meen)$_2Cl_2^+$ and *cis* for *trans*-Co(LL-1,3,8,10-Me_4trien)Cl_2^+), as well as the fact that this effect is essentially similar for these two *trans*-$CoN_4Cl_2^+$ ions which have (*R*)-asymmetric nitrogen.

The difference in the circular dichroism for *trans*-Co(LL-1,3,8,10-Me_4trien)$(NO_2)_2^+$ and *trans*-Co(LL-3,8-Me_2trien)$(NO_2)_2^+$ should have been determined by the vicinal effect from the (*R*)-asymmetric nitrogen. This effect is shown in Figure 7 also and this vicinal effect has positive Cotton effects near 20,800 and 23,500 cm^{-1}. From the Yamatera theory, the lower energy band may be the $^1A_1 \rightarrow {}^1A_2(D_{4h})$ component and the higher energy band may be the $^1A_1 \rightarrow {}^1E(D_{4h})$ component of the $^1A_1 \rightarrow {}^1T_1(O_h)$ d–d transition. The signs of the Cotton effects induced from the (*R*)-asymmetric nitrogen are different for the corresponding component of the *trans*-$CoN_4Cl_2^+$ and *trans*-$CoN_4(NO_2)_2^+$ chromophores.

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The Triamines of Cobalt(III). I. Geometrical Isomers of Trinitrotriamminecobalt(III)[1a]

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A number of preparations from the literature for trinitrotriamminecobalt(III) were examined for their structural arrangement. Evidence for the existence of the facial and meridial isomers was established by proton magnetic resonance spectra and thin layer chromatography and by comparison with other cobalt(III) triamines of known geometry. Additional properties of these isomers studied included their infrared and ultraviolet spectra.

Introduction

In Alfred Werner's classic explanation of the theory of structure of coordination complexes, he submitted considerable evidence for an octahedral arrangement of groups for coordination number of 6. Most important evidence for this structural assignment was that for octahedral complexes containing two different ligands A and B in the general formula MA_nB_{6-n} where $n = 2$, 3, or 4, only two geometrical isomers are possible. Where $n = 2$ (and the equivalent case of $n = 4$), many hundreds of *cis–trans* isomer pairs have been prepared and characterized. However, for $n = 3$, or MA_3B_3, only five such sets of geometrical isomers[2] have been firmly identified: $Ru(H_2O)_3Cl_3$,[3,4] $Pt(NH_3)Br_3^+$,[5] $Pt(NH_3)_3I_3^+$,[6] $Ir(H_2O)_3Cl_3$,[7] and $Rh(CH_3CN)_3Cl_3$.[8] Less clear has been the situation with trinitrotriamminecobalt(III), which was first prepared in 1866 by Erdmann;[9] later preparations were reported by Werner[10] and Jorgensen.[11] No evidence was then given for the structures of these compounds or even whether different isomers were represented. The first study of the various preparations of $Co(NH_3)_3(NO_2)_3$ was reported in 1938[12] by Duval, who examined five methods of preparation by visible, ultraviolet, and infrared spectroscopy, refractive index of aqueous solutions, conductivity, and X-ray powder diffraction. These measurements indicated that two different products resulted when the Werner and Jorgensen preparations were compared. Duval assumed that these were the two geometrical isomers of the complex but he did not assign configurations from his data. In 1952, Tanito, Saito, and Kuroya[13] determined the crystal structure of the product of the Jorgensen preparation to be that of the meridial isomer.

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[1] (a) Presented at the 158th National Meeting of the American Chemical Society, Sept 7–12, New York, N. Y., 1969. (b) Abstracted from the Ph.D. dissertation of R. B. Hagel, Rutgers University, 1969.

[2] The recommended designations for the structures shown in Figure 1 are facial (*fac*) or 1,2,3 and meridial (*mer*) or 1,2,4: R. F. Trimble, *J. Chem. Educ.*, **31**, 176 (1954).

[3] R. E. Connick and D. A. Fine, *J. Am. Chem. Soc.*, **83**, 3414 (1961).

[4] E. E. Mercer and W. A. McAllister, *Inorg. Chem.*, **4**, 1414 (1965).

[5] V. S. Orlova and I. I. Chernyaev, *Zh. Neorgan. Khim.*, **11**, 1338 (1966).

[6] V. S. Orlova and I. I. Chernyaev, *ibid.*, **12**, 1274 (1967).

[7] A. A. El-Awady, E. J. Bounsell, and C. S. Garner, *Inorg. Chem.*, **6**, 79 (1967).

[8] B. D. Catsikis and M. L. Good, *ibid.*, **8**, 1095 (1969).

[9] H. Erdmann, *J. Prakt. Chem.*, **97**, 406 (1866).

[10] A. Werner, *Z. Anorg. Allgem. Chem.*, **15**, 166 (1897).

[11] S. M. Jorgensen, *ibid.*, **17**, 475 (1898).

[12] R. Duval, *J. Pure Appl. Chem.*, **13**, 468 (1938).

[13] Y. Tanito, Y. Saito, and H. Kuroya, *Bull. Chem. Soc. Japan*, **25**, 188 (1952).

Beattie and Tyrrell[14] reported infrared spectroscopic data for a number of nitroamminecobalt(III) complexes including $Co(NH_3)_3(NO_2)_3$ prepared by the Jorgensen method. While they could clearly distinguish between *cis-* and *trans*-dinitrotetraamminecobalt(III) ions, the positions of the absorption bands of $Co(NH_3)_3(NO_2)_3$ at 1320 and 1290 cm^{-1} lie somewhat between the expected values for either the facial or the meridial isomer, although they did accept the Tanito, *et al.*, assignment of meridial structure to their preparation.

A more complete examination of the infrared spectroscopy of these complexes was carried out by Majumdar, Duval, and LeCompte.[15] They concluded that both geometrical isomers did exist and that the Werner preparation yielded the meridial isomer, while the Jorgensen preparation gave the facial form! No mention was made of the X-ray crystal analysis by Tanito, *et al.*[13] Postollec and Mathieu[16] confirmed the two isomers reported by Majumdar, *et al.*, but recognized the previous X-ray structural evidence. In their brief communication, they presented the infrared spectra of the 1,2,4 (*mer*) isomer prepared according to Jorgensen's method and the 1,2,3 (*fac*) isomer prepared by Werner's procedure.

In yet another study of the infrared absorption spectra of a number of cobalt(III) amines and assignment of the observed bands, Maddock and Todesco[17] disputed the earlier claims that the two geometrical isomers had been prepared for $Co(NH_3)_3(NO_2)_3$. They did prepare a nonelectrolyte whose $Co:NH_3:NO_2$ composition analyzed as 1:3:3 and to which they assigned the meridial structure. They presented infrared spectral data for the ionization isomers (*cis*-$Co(NH_3)_4(NO_2)_2)(Co(NH_3)_2(NO_2)_4)$ and (*trans*-$Co(NH_3)_4(NO_2)_2)(Co(NH_3)_2(NO_2)_4)$ and concluded that the facial isomer of Majumdar, Duval, and LeCompte, which would still give the correct chemical analysis, was, in fact, one of the ionization isomers.

In this work, a reexamination of the various methods of preparation of trinitrotriamminecobalt(III) was carried out, and their products were examined by chromatography and paper electrophoresis for evidence of the two geometrical isomers.

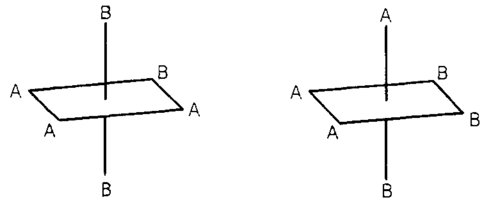
Experimental Section

1. **Preparations.**—The purity criteria used for all of the preparations of cobalt complexes were their analyses by thin layer chromatography and paper electrophoresis. These methods were more sensitive to cobalt-containing impurities than the spectrophotometric methods traditionally used.

***fac*-Trinitrotriamminecobalt(III), $Co(NH_3)_3(NO_2)_3$.**—The method described by Shibata, *et al.*[18] (a method claimed to produce the *mer* isomer), was found to give the best yields. A cold mixture of 7 ml of water with 7 g (0.03 mol) of cobalt(II) chloride hexahydrate and 10 ml of 30% hydrogen peroxide was added dropwise to an ice-cooled slurry of 23 g of potassium hydrogen carbonate in 20 ml of water, and the resulting green solution was quickly filtered.

This solution, containing $Co(CO_3)_3^{3-}$ was cooled in an ice bath and 7 g (0.13 mol) of ammonium chloride, 5 ml (0.07 mol) of 28% aqueous ammonia, and 10 g (0.15 mol) of sodium nitrite were added. This mixture was heated on a steam bath until it turned red-brown. After acidification with 15 ml of 6 *N* acetic acid, the solution was heated for another 30 min. When the solution was allowed to stand overnight in a refrigerator, massive crystals of product were obtained with only a small amount of *cis*-dinitrotetraamminecobalt(III) ion as an impurity. The yield was 1.5 g (21%). *Anal.* Calcd for *fac*-$Co(NH_3)_3(NO_2)_3$: Co, 24.1. Found: Co, 22.9.

***mer*-Trinitrotriamminecobalt(III), $Co(NH_3)_3(NO_2)_3$.**—This procedure was basically that described by Jorgensen[11] (a method claimed to produce the *fac* isomer), as modified by Cooley, Liu, and Bailar[19] to improve the purity of the product. A solution of 90 g (0.38 mol) of cobalt(II) chloride hexahydrate in 250 ml of water was added to a solution containing 100 g (1.85 mol) of ammonium chloride, 135 g (1.95 mol) of sodium nitrite, and 345 ml of 28% aqueous ammonia in 900 ml of water. A rapid stream of air was bubbled through the mixture for 4 hr. The solution was evaporated under an air jet to half its original volume. The resulting crystalline product was suction filtered, washed with cold water, ethanol, and ether, and air dried. The crude product was thoroughly ground in a mortar and again placed on a suction filter. Twelve 25-ml portions of cold water were successively poured over the crystals and suctioned off to remove ammonium chloride. Recrystallization was carried out by pouring successive 200-ml portions of 1.5 *M* acetic acid at 60° onto the product, stirring, and filtering. The treatment was continued until about 5 g of material remained. From 5 to 7 l. of acid was required. The solid on the filter, consisting mostly of the ionization isomer $(Co(NH_3)_4(NO_2)_2)(Co(NH_3)_2(NO_2)_4)$, was discarded. The combined filtrates were evaporated to half their original volume under an air jet. The recrystallized complex was filtered, dried, and ground, then washed with water, ethanol, and ether, and air dried. The yield was 21 g (24%). *Anal.* Calcd for *mer*-$Co(NH_3)_3(NO_2)_3$: Co, 24.6. Found: Co, 23.5.



a. MERIDIAL b. FACIAL

Figure 1.—Isomers of CoA_3B_3.

Purification of *fac*- and *mer*-$Co(NH_3)_3(NO_2)_3$.—Both preparations still contained measurable amounts of cobalt-containing impurities so that further treatment was required for samples used for spectroscopic experiments. Taking advantage of the limited solubility of these complexes in acetone compared to the insolubility of the principal contaminant, the ionization isomer, about 500 mg of starting material was extracted with three 10-ml portions of reagent grade, dry acetone. This extraction left in the residue most of the ionic impurities. The extracts were combined and reduced in volume to about 5 ml.

A small chromatographic column was constructed of 8-mm o.d. Pyrex tubing packed to a depth of 10 cm with silica gel H (Brinkman Instruments, Westbury, N. Y.), activated at 110° for 20 min, and wet with acetone after it had cooled. The acetone extract of the complex was placed at the top of the column, about 25 ml of acetone was added, and air pressure from the laboratory line was applied to the top of the column. The first 30% of the eluent contained some anionic cobalt(III) complexes

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[14] I. R. Beattie and H. J. V. Tyrrell, *J. Chem. Soc.*, 2849 (1956).

[15] A. K. Majumdar, C. Duval, and J. LeCompte, *Compt. Rend.*, **247**, 302 (1958).

[16] M. L. Postollec and J. P. Mathieu, *ibid.*, **257**, 3185 (1963).

[17] A. G. Maddock and A. B. J. B. Todesco, *J. Inorg. Nucl. Chem.*, **26**, 1535 (1964).

[18] M. Shibata, M. Mori, and E. Kunyo, *Inorg. Chem.*, **3**, 1573 (1964).

[19] W. E. Cooley, C. F. Liu, and J. C. Bailar, *J. Am. Chem. Soc.*, **81**, 4189 (1959).

and was discarded. The remaining eluent, which required 2–5 min to pass through the column, was collected and evaporated to dryness under an air stream. Any cationic impurities remained as a band at the top of the column. Trinitrotriamminecobalt(III) purified in this manner produced a yield in which no other cobalt-containing impurities could be detected by thin layer chromatography. From the sensitivity of the analysis, an estimate of the purity is 99.9%.

mer-Trinitrotris(methylamine)cobalt(III), $\mathbf{Co(CH_3NH_2)_3(NO_2)_3}$.[20]—A 170-ml sample of 25% methylamine and 50 ml of dilute acetic acid were added to 30 g of sodium hexanitrocobaltate(III) dissolved in 300 ml of water. The mixture was stirred vigorously for 1 hr after which the pH was adjusted to 5–6 by the addition of 35 ml of glacial acetic acid. After 2–3 hr, pale yellow crystals were deposited, but the mixture was left overnight in order to complete the crystallization. The product was suction filtered, washed with cold water, alcohol, and air dried. The yield was 8.5 g (38%). *Anal.* Calcd for *mer*-$Co(CH_3NH_2)_3(NO_2)_3$: Co, 20.6. Found: Co, 19.2.

mer-Trinitrodiethylenetriaminecobalt(III), Co(dien)$(NO_2)_3$, was prepared by the method devised by Crayton and Mattern.[21]

cis- and _trans_-dinitrotetraamminecobalt(III) nitrates ($Co(NH_3)_4(NO_2)_2)(NO_3)$, were prepared by the direction of Schlessinger.[22]

2. **Thin Layer Chromatography.**—Thin layer chromatography was run on precoated, preactivated silica gel plates, Type Q-1, with *starch* binder (Quantum Industries, Fairfield, N. J.), as supplied by the manufacturer. Sample sizes of 1–4 μl of either acetone or dimethyl sulfoxide (DMSO) solutions of the complexes were applied and the chromatograms were developed.

To separate cobalt(III) complexes of different charge, a solvent system of CH_3OH–DMSO–$HClO_4$ (60:40:0.1) was used. Results were similar to those reported earlier.[23] In this solvent system, anionic complexes ran with the solvent front, and neutral complexes ran near the solvent front, while cationic complexes trailed, depending on their charge and geometry.

To separate the geometrical isomers of $Co(NH_3)_3(NO_2)_3$, acetone was found to be the most effective solvent. Table I lists the R_f values of the various complexes as well as ratios of R_f/R_f(*mer* isomer). R_f values were found to be very sensitive to conditions of development while the ratios were always reproducible to ±0.02.

TABLE I

THIN LAYER CHROMATOGRAPHY OF SOME COBALT(III) NITROAMINES[a]

Complex	R_f	R_f/R_f(*mer* isomer)
mer-$Co(NH_3)_3(NO_2)_3$	0.76	1.00
mer-$Co(CH_3NH_2)_3(NO_2)_3$	0.85	1.15
mer-Co(dien)$(NO_2)_3$	0.80	1.05
fac-$Co(NH_3)_3(NO_2)_3$	0.62	0.82
$Co(NH_3)_2(NO_2)_4^-$	1.00	1.30
cis-$Co(NH_3)_4(NO_2)_2^+$	0.08	0.1
trans-$Co(NH_3)_4(NO_2)_2^+$	0.08	0.1

[a] Solvent, acetone; adsorbants, silica gel Q-1.

The developed plates were sprayed with a water–alcohol solution of nitroso-R sodium salt and heated to 110° for 15 min. In some cases, it was necessary for the plates to stand for 2–3 days for certain of the complexes to develop a color. The cobalt appeared as an orange spot against a pale yellow background.

3. **Electrophoresis.**—Paper electrophoresis was carried out on a Research Specialties chamber on 20 × 50 cm Whatman No. 1 paper. The electrolyte was 0.01 *M* NH_4NO_3. Samples (1–4 μl) were spotted midway between the two electrodes and the system was electrolyzed for 1 hr by a 475-V dc, a current of 4–4.5 mA. Trials at various voltages showed that below 350 V, no movement of the complexes took place while above 500 V, several of the less stable complexes underwent decomposition. Table II lists migration rates for some of the complexes. The sign indicates the polarity of the electrode toward which migration took place.

TABLE II

ELECTROPHORESIS MIGRATION RATES OF SOME COBALT(III) NITROAMINES

Complex	Migration rate, mm/hr	Complex	Migration rate, mm/hr
mer-$Co(NH_3)_3(NO_2)_3$	0	$Co(NH_3)_2(NO_2)_4^-$	+95
mer-$Co(CH_3NH_2)_3(NO_2)_3$	0	$Co(NO_2)_6^{3-}$	+143
mer-Co(dien)$(NO_2)_3$	0	*cis*-$Co(NH_3)_4(NO_2)_2^+$	−92
fac-$Co(NH_3)_3(NO_2)_3$	0	*trans*-$Co(NH_3)_4(NO_2)_2^+$	−91

4. **Spectrophotometry.**—Visible and ultraviolet spectra of the complexes were measured with a Cary Model 14 spectrophotometer, in matched 10-mm silica cells. Solvents used were water, acetone, and DMSO.

Infrared spectra were determined with a Beckman Model IR-10 spectrophotometer using Nujol mulls, KBr disks, and disks of pure complex. The Nujol mulls and KBr disks gave identical spectra for the complexes. While there is reason to doubt the reliability of the spectra obtained from the pure-complex disks, samples run in KBr pellets when the sample concentration was varied from 1 to 60% showed no change in spectra. The use of the disks of pure complex greatly enhanced the spectra in the 400–600-cm^{-1} region.

5. **Proton Magnetic Resonance Spectra.**—Pmr spectra were measured with a Varian A-60 instrument at a frequency of 60 MHz at 25°. Sweep rates of 250 Hz/sec and sweep widths of 250 and 500 Hz were used. Samples were dissolved in DMSO (concentrations of *ca.* 5% by weight) and run against a TMS external standard.

Discussion and Results

I. Examination of the Methods of Preparation.—The principal methods of preparation of trinitrotriaminecobalt(III)[10,11,18,19,24,25] were examined for the geometry of the trinitrotriammine formed and for the principal impurities by thin layer chromatography and paper electrophoresis. Table III lists these preparations and the identity of the products before purification by the acetone extraction and chromatography.

TABLE III

ANALYSIS OF VARIOUS PREPARATIVE METHODS FOR $Co(NH_3)_3(NO_2)_3$

Ref	Primary product	Impurities
10	*fac*-$Co(NH_3)_3(NO_2)_3$	$Co(NH_3)_2(NO_2)_4^-$
22, 24	*fac*-$Co(NH_3)_3(NO_2)_3$	*cis*-$Co(NH_3)_4(NO_2)_2^+$ $Co(NH_3)_2(NO_2)_4^-$
18[a]	*fac*-$Co(NH_3)_3(NO_2)_3$	*cis*-$Co(NH_3)_4(NO_2)_2$[a] $Co(NH_3)_5(NO_2)^{2+}$
11[b]	*mer*-$Co(NH_3)_3(NO_2)_3$	*trans*-$Co(NH_3)_4(NO_2)_2$[a] *cis*-$Co(NH_3)_4(NO_2)_2^+$ $Co(NH_3)_2(NO_2)_4^-$
19	*mer*-$Co(NH_3)_3(NO_2)_3$	*trans*-$Co(NH_3)_4(NO_2)_2$[a] *cis*-$Co(NH_3)_4(NO_2)_2$[a] $Co(NH_3)_2(NO_2)_4^-$

[a] Claimed to produce *mer* isomer. [b] Claimed to produce *fac* isomer.

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(20) I. I. Chernyaev, A. G. Ganiev, Sh. Sh. Tarkhtaev, and Sh. Sh. Rizaeva, *Zh. Neorgan. Khim.*, **13**, 157 (1968).

(21) P. H. Crayton and J. H. Mattern, *J. Inorg. Nucl. Chem.*, **13**, 248 (1960).

(22) G. G. Schlessinger, "Inorganic Laboratory Preparations," Chemical Publishing Co., New York, N. Y., 1962, p 246.

(23) (a) L. F. Druding and R. B. Hagel, *Anal. Chem.*, **38**, 478 (1966); (b) R. B. Hagel and L. F. Druding, *Separ. Sci.*, **4**, 89 (1969).

(24) W. G. Palmer, "Experimental Inorganic Chemistry," Cambridge University Press, London, 1954, p 539.

(25) Reference 22, p 262.

The nature of the impurities in each of these preparations is consistent with its structural assignment. In all of the five methods examined, only one isomer of $Co(NH_3)_3(NO_2)_3$ was produced. Preparations which lead to the *facial* isomer contained only the *cis* form of the dinitrotetraammine while the two methods of preparing the meridial isomer contained both the *cis*- and *trans*-dinitrotetraammine ions. The conditions of synthesis of *fac*-$Co(NH_2)_3(NO_3)_3$ are almost identical with those of the *cis*-dinitro complex: solutions are heated above 60° after oxidation while the complex forms. In the preparation of the meridial isomer, as in the synthesis of the *trans*-dinitro complex, formation of the complex is from solutions at or near room temperature.

It was not possible to identify the geometry of the tetranitrodiamminecobalt(III) ion in these preparations. Where the anionic complex was observed, it was assumed to be part of the ionization isomer, whose solubility in water is as low as that of the trinitrotriammine. Only in the Werner preparation did the ionization isomer appear in large quantities as an impurity. The most important criteria in the formation of the trinitrotriamminecobalt(III) complex and one that is most important for a reasonable yield is that the molar ratios of ammonia and ammonium ion to nitrite be equal. The only impurity then is the ionization isomer. Indeed, Shibata, *et al.*,[18] demonstrated that complexes from nitropentaamminecobalt(III) to hexanitrocobaltate(III) could be prepared from tris(carbonato)cobaltate(III) ion by the same experimental procedure wherein only the concentrations of ammonia to nitrite were varied.

The facial isomer is much less stable than the meridial isomer, decomposing in solution or in the solid to the ionization isomer. In DMSO solution, decomposition was essentially complete in 3–4 hr, while in the solid, complete decomposition required about 2–3 weeks. The meridial isomer showed only a slight tendency to decompose in solution and was indefinitely stable in the solid state. Majumdar, Duval, and LeCompte[15] may well have prepared both isomers, but by the time they measured the infrared spectra the conversion to the ionization isomer could have been completed, thereby accounting for Maddock and Todesco's disputation.[17]

II. Identification of the Geometrical Isomers. A. Proton Magnetic Resonance Spectra.—Aside from X-ray crystallographic analysis which was not attempted in this work, the proton magnetic resonance spectra provide the most definitive method of differentiating between the two isomers.

The facial isomer has three equivalent ammine groups, whose proton interactions should show up as a single peak, while the meridial isomer contains two ammines *trans* to one another and a third ammine that is *trans* to a nitro group. In this latter complex, two peaks whose area ratio is 2:1 should be observed.

Because quadrapole coupling of the ammine protons with the nitrogen nucleus causes considerable line broadening, the first pmr measurements were made with trinitrotris(methylamine)cobalt(III) where both amine protons and the methyl protons should be observed, but, more importantly, the methyl protons should be more easily discernible. This complex was first prepared by Chernyaev, *et al.*,[20] and reported by them to be the meridial isomer based on solubility data, refractive indices of aqueous solutions, and X-ray powder diagrams which were similar to the *mer*-trinitrotriamminecobalt(III).[26] Following their procedure for the methylamine complex, a pure product, containing only one geometrical isomer was obtained. The pmr spectrum of the complex dissolved in DMSO is shown in Figure 2. Solvent bands have been eliminated from this tracing. The peaks from the methyl protons show up sharply as a pair of overlapping triplets at δ 1.52 and 1.63 ppm in the expected area ratio of 1:2. The amine protons appear as two bands at δ 3.72 and 4.08 in the ratio of 1:2, clearly establishing this complex as the meridial isomer.

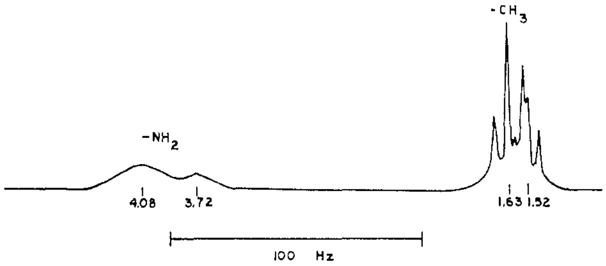

Figure 2.—The 60-MHz proton spectrum of *mer*-$Co(CH_3NH_2)_3(NO_2)_3$.

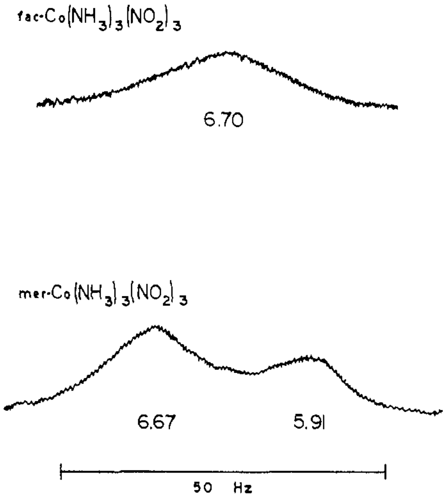

Figure 3.—The 60-MHz proton spectra of $Co(NH_3)_3(NO_2)_3$ isomers.

Figure 3 shows the pmr spectra of the facial and meridial isomers of $Co(NH_3)_3(NO_2)_3$. The initial assignment of their geometrical configurations had been based on their R_f values from thin layer chromatography. This assignment was confirmed by the pmr spectra. The facial isomer shows a single, broad peak

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[26] A. Ganiev, *Zh. Neorgan. Khim.*, **7**, 261 (1962).

at 6.7 ppm while the meridial isomer has two bands at 5.91 and 6.67 ppm whose area ratio is 1:2.

B. Thin Layer Chromatography.—Based on observations of other cobalt(III)–amine complexes[23] using acidic solvents on silica gel adsorbants, R_f values for the complexes were observed to increase as the charge on the complex decreased. Further, it was possible to distinguish between *cis* and *trans* isomers of the type $Co_4B_2^+$ from their relative R_f values. Since the *cis* isomer has a charge polarization that the *trans* isomer lacks, it is more strongly adsorbed on the silica gel. By this argument, the facial isomer of the neutral complex $Co(NH_3)_3(NO_2)_3$ should have a lower R_f than the meridial isomer because it has a higher dipole moment. It was this assumption, coupled with the X-ray crystallographic analysis of the Jorgensen preparation, that led to the original assignment of configuration of these complexes. Comparing R_f values in Table I, the meridial isomers of the various complexes have quite similar R_f values. Insufficient samples of known facial complexes were available for comparison of these R_f values. Crayton and Mattern[21] assigned the meridial structure to Co(dien) $(NO_2)_3$ by its similarity of its uv–visible absorption spectra to that of $Co(NH_3)(NO_2)_3$, a method which we found to be unreliable. Nevertheless, the thin layer chromatograms of this complex resulted in R_f values compatible with other meridial complexes. In one or two fresh preparations of this complex, a second faint spot could be seen at R_f 0.6–0.7 which may have been the facial isomer of the diethylenetriamine complex.

C. Electronic Absorption Spectra.—The visible and ultraviolet spectra of the facial and meridial isomers of $Co(NH_3)_3(NO_2)_3$ are presented in Figure 4. Both complexes are yellow in the solid state or in solution. Both isomers have a similar spectrum in the visible region, although the nonsymmetrical appearance of the absorption band at 350 mμ suggests that it might represent several overlapping bands. From the similarity of molar extinction coefficients for these two complexes over most of the visible and ultraviolet regions, the inadvisability of using these spectral methods of differentiating between the two complexes may be understood. Additionally, a common impurity, the ionization isomer $(Co(NH_3)_4(NO_2)_2)(Co(NH_3)_2(NO_2)_4)$ is yellow and has similar extinction coefficients in the visible region. Use of the d–d transition in the visible and near-ultraviolet region has been quite effective in differentiating between *cis*- and *trans*-MA_4B_2, and should be equally effective for identifying *fac*- and *mer*-MA_3B_3. If one considers the dipoles along the three coordinate axes, the *fac* isomer has cubic symmetry while the *mer* isomer has rhombic symmetry.[27] From the splitting of the energy levels of the 3d electrons of cobalt(III), two bands ($A_{1g} \rightarrow T_{1g}$, $A_{1g} \rightarrow T_{1g}$) would be expected for *fac*-$Co(NH_3)_3(NO_2)_3$ while six would be expected for the *mer* isomer where the T_{1g} and T_{2g} levels are further split. In *mer*-$Co(NH_3)_3(NO_2)_3$ the splitting has not been sufficient to generate separate bands and indeed the shoulders of the band at 350 mμ are only slightly more pronounced then the broadening of the same band of the *fac* isomer. This splitting effect could easily be obscured by impurities such as the ionization isomer and dinitrotetraammine or nitrotriammine complexes, all of which have absorption maxima in this region.

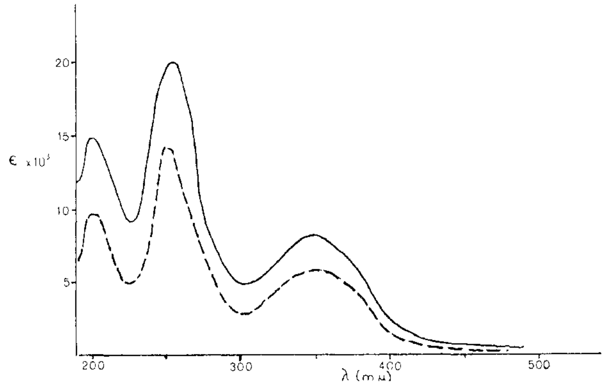

Figure 4.—Visible and uv spectra of $Co(NH_3)_3(NO_2)_3$ isomers: ——, *mer;* - - -, *fac.* The solvent is H_2O.

The intensity of the d–d absorption band has also been used to distinguish between geometrical isomers where *cis*-MA_4B_2 has a higher extinction coefficient for the transition than do the *trans* isomers. In the case of $Co(NH_3)_3(NO_2)_3$, while the less symmetrical form does have the high extinction coefficient, there are MA_3B_3 complexes where this is not observed.[4,7] Recently, Demas, Turner, and Crosby[28] used the charge-transfer band in the ultraviolet region to identify the *cis* isomer of $Ru(py)_4Cl_2$, where py is pyridine. They proposed that there is a relationship between the energy of the electronic absorption spectrum and the Kosower *Z* values[29] for the solvents used. Compounds with a permanent dipole moment should show shifts that are linear with their Kosower *Z* values while those without a permanent dipole should have their charge-transfer bands unaffected. In the case of the ruthenium complexes of Demas, *et al.*, the *cis* isomer has a permanent dipole while the *trans* isomer does not.

This type of measurement was attempted for the *fac*- and *mer*-$Co(NH_3)_3(NO_2)_3$ where both complexes have permanent dipole moments[30] but the dipole moment of the former would be expected to be the greater. Because the nature of the solvent interaction with either the ground state or the excited state in the charge-transfer energy change has not been established, the effect of solvent change on the location of the charge-transfer band could not be predicted. Most

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(27) (a) J. Lewis and R. G. Wilkins, "Modern Coordination Chemistry," Interscience Publishers, New York, N. Y., 1960, p 188; (b) C. J. Ballhausen and C. K. Jørgensen, *Kgl. Danske Videnskab. Selskab, Mat. Fys. Medd.*, **29**, No. 14 (1955).

(28) J. N. Demas, T. F. Turner, and G. A. Crosby, *Inorg. Chem.*, **8**, 674 (1969).

(29) E. M. Kosower, *J. Am. Chem. Soc.*, **80**, 3253 (1958).

(30) Measurement of the dipole moments of these complexes by the dielectric constant method was not attempted. These complexes were not soluble in solvents of low dielectric strength where their differences in dipole moments would be enhanced. In such solvents as DMSO and water, their solubilities are small enough so that error in measurement or the presence of trace amounts of ionic impurities could easily exceed the expected differences in dielectric constant.

likely, the facial isomer with its larger dipole, should show a greater shift in its band location. A second limitation to this study was the limited number of solvents for these complexes. Two of the best solvents, acetone and DMSO, are opaque in the region of the charge-transfer band. Nevertheless, the spectra of the two isomers were measured in methanol and water, whose Kosower Z values are 83.6 and 94.6, respectively, for the meridial isomer; the band at 255 mμ showed no change between methanol and water, while the *facial* isomer band at 258 mμ in methanol appeared at 250 mμ in water. This seems to indicate that the dipole moment of the meridial isomer is quite small.

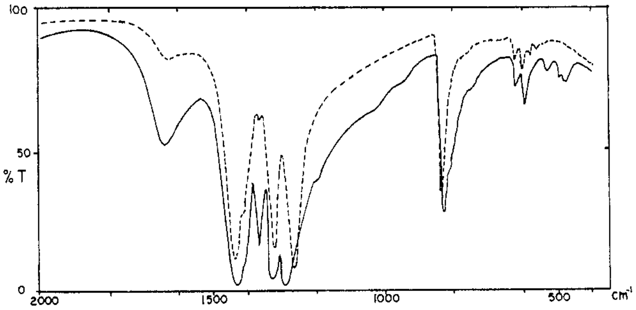

Figure 5. Ir spectra of $Co(NH_3)_3(NO_2)_3$ isomers: ——, *mer;* - - -, *fac.*

TABLE IV

INFRARED ABSORPTIONS OF SOME COBALT(III) TRINITROAMINES[a]

	$Co(NH_3)_3(NO_2)_3$ *fac*	$Co(NH_3)_3(NO_2)_3$ *mer*	*mer*-$Co(CH_3NH_2)_3(NO_2)_3$	*mer*-Co(dien)-(NO_2)
	1640 m	1650 m	1605 m	
			1565 w	1585 m
				1500 w
			1486 vw	1470 w
	1426 s	1432 s	1421 s	1432 s
$\nu(NO_2)_a$	1401 vw	1408 w	1399 s	1395 m
$\nu(NO_2)_s$	1368 m	1370 vw	1368 m	1368 m
$\delta(NO_2)_s$	1330 s	1332 s	1321 s	1325 s
$[\nu(NO_3^-)]$		1295 vw	1302 w	
	1290 s	1270 s	1259 w	1262 m
			1223 m	1145 m
				1105 m
			1073 s	1070 w
			1030 w	1050 w
			1009 vw	947 w
				910 vw
				880 w
				860 w
$\delta(NO_2)_s$	825 m	832 s	826 s	838 s
			732 vw	752 w
			710 w	
			665 w	629 w
		625 w		615 w
$\delta(NO_2)_w$	610 m	605 m	604 m	
	586 m	565 vw	590 vw	585 w
			560 w	
	520 w	508 w		535 w
$\nu(CO–N(NH_3))$	485 vw	490 vw	500 w	508 w
	472 w		450 w	

[a] Abbreviations: s, strong; m, medium; w, weak; vw, very weak.

D. Infrared Absorption Spectra.—The infrared spectra of the two isomers are presented in Figure 5 and summarized in Table IV. Nakagawa and Shimanouchi[31] studied a number of cobalt(III) nitroammines, comparing calculated and experimental values of their vibrational energy bands, including *mer*-$Co(NH_3)_3(NO_2)_3$. The spectrum observed in this work for the meridial isomer agrees with that of Nakagawa and Shimanouchi to within ±7 cm^{-1}. As the instrument used for these measurements is estimated to have an accuracy of ±5 cm^{-1}, this agreement is considered quite good. Of particular interest is the comparison of these results with those of Postollec and Mathieu.[16] Agreement with their reported meridial isomer is good, although in the region 1300–1500 cm^{-1} their results are 20–30 cm^{-1} lower. Even accounting for this difference, agreement with their reported spectrum of the facial isomer is not as good. In the region 400–600 cm^{-1}, the present results show a greater number and more distinctive peaks.

As might be expected from symmetry arguments, the more symmetrical facial isomer has a slightly less complex spectrum than the meridial isomer. As was observed for the cobalt(III) tetraammines, an increase in symmetry is also accompanied by a shift in absorption bands to higher wave numbers. This can be best seen in the $\delta(NO_2)_w$ band which is at 610 cm^{-1} for *mer*-$Co(NH_3)_3(NO_2)_3$ and at 625 cm^{-1} for the *fac* complex. The $\delta(NO_2)_s$ band shows a shift from 825 cm^{-1} for *mer* to 832 cm^{-1} for *fac*. The approximate modes of vibration in Table IV are those assigned by Nakagawa and Shimanouchi. Also included in Table IV are the spectra of *mer*-$Co(CH_3NH_2)_3(NO_2)_3$ and *mer*-Co(dien)(NO_2) to show the similarities of the various meridial complexes. Each of these is characterized by a sharp band at 1368 cm^{-1} which is absent in *fac*-$Co(NH_3)_3(NO_2)_3$. Also, the triammine and tris-methylamine complexes exhibit similar nitro

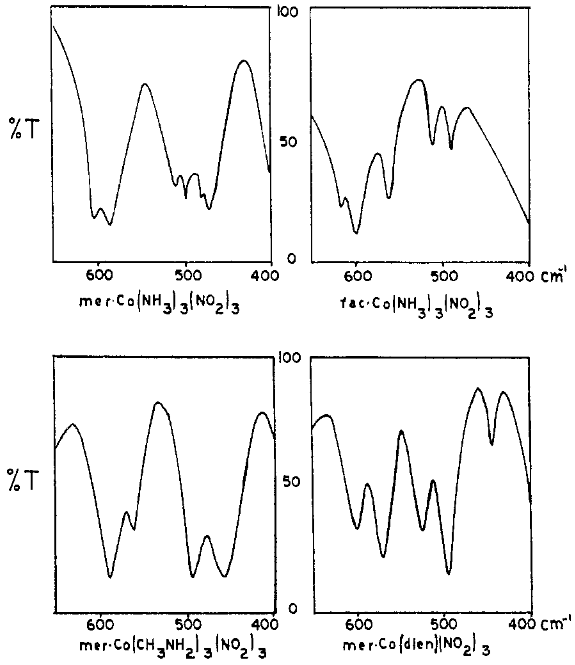

Figure 6.—Ir spectra of Co(III) compounds.

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[31] I. Nakagawa and T. Shimanouchi, *Spectrochim. Acta*, **23A**, 2099 (1967).

stretching frequencies in the 1200–1500-cm^{-1} region and $\delta(NO_2)_s$ at 825 cm^{-1}.

Figure 6 compares the infrared spectra of the four complexes in the 400–600-cm^{-1} region as measured on disks of pure complex. The three meridial isomers show a very similar pattern of bands, with especially strong doublets at 600 and 500 cm^{-1} due to $\delta(NO_2)_w$ and $\nu(Co{-}N(NH_3))$, respectively.

As previously noted by Nakagawa and Shimanouchi, the values of the observed and calculated spectra of *mer*-$Co(NH_3)_3(NO_2)_3$, while in fair agreement, are not exactly the same because of the oversimplified assumption of the C_{2v} model for the complex. One must therefore expect a lower order of symmetry for either or both isomers of $Co(NH_3)_3(NO_2)_3$ and should not rely as heavily on infrared data for the purpose of identification as one does for the *cis–trans* isomers.

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The Magnetic Properties of Hexaamminecobalt(III) Pentachlorocuprate(II)

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The magnetic susceptibility of hexaamminecobalt(III) pentachlorocuprate(II) has been measured from 2.4 to 38°K. The susceptibility obeys the Curie–Weiss law, $\chi = C/(T + \Theta)$, in the temperature range 16–38°K, giving an effective magnetic moment of 1.95 BM with $\Theta = 17$°K. There is an antiferromagnetic transition near 8°K attributed to an intermolecular cation–anion–anion–cation mechanism.

Introduction

In the first report of the magnetism of the pentachlorocuprate(II) ion, Mori[2] noted that susceptibility data for $[Co(NH_3)_6][CuCl_5]$ obeyed the Curie–Weiss law from 4.2 to about 2°K, giving a magnetic moment of 1.47 BM. Our subsequent studies[3] in the temperature range 77–300°K yielded a magnetic moment of 1.85 BM. Because the $2A_1'$ ground electronic state[3,4] of the trigonal-bipyramidal $CuCl_5^{3-}$ ion is not expected to show a decrease in moment at low temperature, the magnetic properties of $[Co(NH_3)_6][CuCl_5]$ in the intervening temperature range need to be determined. Here we report the results of measurements from 2.4 to 38°K.

Experimental Section

Preparation of $[Co(NH_3)_6][CuCl_5]$.—Large, well-formed, orange crystals of hexaamminecobalt(III) pentachlorocuprate(II) were deposited from an aqueous solution (200 ml) of $[Co(NH_3)_6]Cl_3$ (2 g) and $CuCl_2 \cdot 2H_2O$ (10 g). *Anal.* Calcd for $[Co(NH_3)_6][CuCl_5]$: Cl, 44.24; N, 20.86; H, 4.50. Found: Cl, 44.23; N, 20.79; H, 4.47.

Magnetic Susceptibility Determinations.—The magnetic properties of a powdered sample of $[Co(NH_3)_6][CuCl_5]$ (0.16177 g) in a plastic sample holder were determined with a Foner-type vibrating sample magnetometer[5] built by Princeton Applied Research Corp. Measurements were made at magnetic field strengths of 2000 and 10,000 Oe. The magnetometer was calibrated with a sphere of pure nickel metal. Correction was made for the diamagnetism of the sample holder assembly.

Results

The temperature variation of the inverse magnetic susceptibility of $[Co(NH_3)_6][CuCl_5]$ from 2.4 to 38°K is shown in Figure 1. The molar susceptibilities were calculated from the experimental observations after correction for (a) the diamagnetism (244×10^{-4} cgsu) of the constituent atoms using Pascal's constants and (b) the temperature-independent paramagnetism of the hexaamminecobalt ion (75×10^{-6} cgsu).[6] For temperatures above 16°K the susceptibility exhibits a Curie–Weiss behavior with an effective moment of 1.95 BM and a paramagnetic Curie temperature of 17°K. A single smooth curve fits the magnetic moments determined between 2.4 and 38°K by the vibrating sample magnetometer and the magnetic moments determined between 77 and 300°K by the Faraday method.[3]

The differences noted in Figure 1 between runs 1 and 2 are an indication of the precision and accuracy of the magnetic measurements. Thus, the magnetic moment calculated from the slope of either set of magnetic data is more reliable than a moment calculated from a line fitted to the data obtained in both

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[1] ORAU Research Participant.

[2] M. Mori, *Bull. Chem. Soc. Japan*, **34**, 454 (1961).

[3] W. E. Hatfield and T. S. Piper, *Inorg. Chem.*, **3**, 841 (1964).

[4] W. E. Hatfield, H. D. Bedon, and S. M. Horner, *ibid.*, **4**, 1180 (1965).

[5] S. Foner, *Rev. Sci. Instr.*, **30**, 548 (1959).

[6] The susceptibility of $[Co(NH_2)_6]Cl_3$ was taken to be -87.7×10^{-6} cgsu: G. Foex, "Constants Selectionnees Diamagnetisme et Paramagnetisme," Masson and Co., Paris, 1957, p 43. The diamagnetic susceptibility for $[Co(NH_3)_6]Cl_3$ calculated from Pascal's constants is -163×10^{-6} cgsu, and the difference between the two was taken to be TIP for $Co(NH_3)_6^{3+}$ ion.