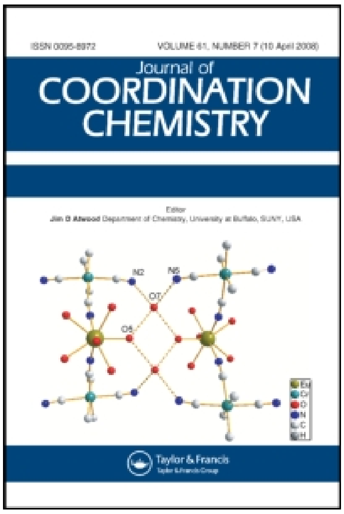

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Leonard F. Druding[a]; Hsien-Chang Wang[a]; Robert E. Cohen[a]; Fred D. Sancilio[a]
[a] Department of Chemistry, Rutgers University, Newark, N.J.

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THE TRIAMINES OF COBALT[III]. II. INFRARED AND NUCLEAR MAGNETIC RESONANCE SPECTRA OF SOME AZIDO COMPLEXES.[1]

LEONARD F. DRUDING, HSIEN-CHANG WANG, ROBERT E. COHEN and FRED D. SANCILIO

Department of Chemistry, Rutgers University, Newark, N.J. 07102

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Recent studies(1) have investigated the formation and properties of the geometrical *facial* and *meridional* isomers of the triamine complexes of cobalt[III]. While identification of the geometrical isomers of some cobalt[III] complexes with diethylenetriamine [dien] was possible using infrared spectroscopy(2, 3), such was not the case with $[Co[NH_3]_3[NO_2]_3]$ where proton magnetic resonance spectroscopy provided confirmation of structure. Attention was turned to the azido complexes of cobalt[III] where $[Co[NH_3]_3[N_3]_3]$,(4) $[Co[dien][N_3]_3]$,(5) and $[Co[dpt][N_3]_3]$(6) [dpt = dipropylenetriamine] have been prepared. Linhard and Weigel reported their preparation of $[Co[NH_3]_3[N_3]_3]$ to have meridional geometry based on chemical evidence. In the later two complexes, no structure was reported. This investigation was undertaken to determine if a *facial* isomer of either triazidotriamminecobalt[III] or triazidodiethylenetriaminecobalt[III] could be prepared. Identification by analysis of the infrared spectra of these complexes is less reliable than other methods because of the relatively small anticipated spectral differences. Also, not much has been reported on the infrared absorptions of coordinated azide ligands(7–12).

EXPERIMENTAL

A. *Spectra* Infrared spectra were measured on a Beckman Model IR-10 spectrophotometer with samples in a KBr pellet. Several samples were also run in a Nujol mull to verify a lack of exchange between bromide and azide during compression of the KBr. Visible spectra were measured on a Cary Model 14 spectrophotometer.

Proton magnetic resonance spectra were recorded on both Varian Model A-60 and Varian Model HA-100 spectrometers. The samples were dissolved in d_6-DMSO and an internal of TMS standard was used.

B. *Preparations* WARNING: THE AZIDO COMPLEXES OF COBALT ARE DETONATORS, ESPECIALLY SENSITIVE AT ELEVATED TEMPERATURES!! USE EXTREME CAUTION WHEN HANDLING THE DRY SALTS!!

1. Azidopentaamminecobalt(III) chloride, $[Co[NH_3]_5N_3]Cl_2$—method of Linhard and Flygare.(13)

2. *Cis* and *trans*-diazidotetraamminecobalt[III] chloride, $[Co[NH_3]_4[N_3]_2]Cl$—method of Linhard and Flygare.(13)

3. *Cis* and *trans*-diazidobis[ethylenediamine]cobalt[III] chloride, $[Co[en]_2[N_3]_2]Cl$—method of Staples and Tobe.(8)

4. Triazidotriamminecobalt(III), $[Co[NH_3]_3[N_3]_3]$—method of Linhard and Weigel:(4) 5.4 g [0.045 mole] of cobalt[II] carbonate[reagent grade] and 5 g [0.088 mole] ammonium sulfate were dissolved in 100 ml water and 3 ml conc. sulfuric acid. After dissolution, 60 ml 20% aqueous ammonia was slowly added, then 14 g [0.21 mole] sodium azide. Air was bubbled through the solution for two hours, following which the solution was evaporated to near dryness on a steam bath. The red solution gave way to a greenish-brown solid. WARNING: THIS EVAPORATION SHOULD BE CARRIED OUT BEHIND A SAFETY SHIELD AS THE HOT EVAPORATES ARE EXTREMELY SHOCK SENSITIVE. THEY SHOULD NOT BE TOUCHED UNTIL COOLED TO ROOM TEMPERATURE! The residue was carefully transferred to a Buchner funnel. DO NOT TRY TO SCRAPE ANY SOLID THAT ADHERES TO THE BEAKER. The solid was washed with portions of cold water until the filtrate was green, then washed with methanol and air-dried. The yield of dark green crystalline solid was 8.1 g [76% theor. based on $CoCO_3$]. Analysis: found: Co-24.6%, N-69.0%, H-3.78%, theor.: Co-24.9%, N-71.2%, H-3.81% [Note: nitrogen and hydrogen analysis were run on F & M Model 185 Analyzer which resulted in exceedingly fast decomposition of sample with some loss of nitrogen.]

Other less hazardous procedures were used for the synthesis of this compound, but all gave the same isomeric form in lower yields. The procedure described above was the only one which gave single crystals suitable for X-ray crystallographic studies now in progress.

5. Azidooxalatotriamminecobalt[III], $[Co[NH_3]_3[C_2O_4][N_3]]$—2.0 g triazidotriamminecobalt[III] was added to 20 ml water, followed by the addition of 2 g oxalic acid. The mixture was heated on a steam bath during which the green color of the triazido complex gave way to a purple color. After about 30 min., the mixture was cooled in an ice-water bath, and 40 ml 95% ethanol was added to complete the precipitation. The product was suction filtered, washed with alcohol, then ether, and air-dried. Yield of purple powder was 2.1 g. Analysis: found: Co-24.4%, N-34.2%, C-9.9%, theor.: Co-24.6%, N-24.6%, N-35.0%, C-10.0%.

6. Azidodinitrotriamminecobalt[III], $[Co[NH_3]_3[NO_2]_2[N_3]]$—One gram of chlorodinitrotriamminecobalt[III]^(14) and 0.5 g sodium azide was added to 10 ml water and the mixture was heated on a steam bath for 90 minutes. There was no observable change in color. After cooling in an ice-water bath, the mixture was filtered, washed with alcohol, then ether and air-dried. A brown powder, yield of 0.7 g, was recovered. Analysis: found: Co-23.9%, N-44.3%, H-3.67%, theor.: Co-24.1%, N-45.9%, H-3.69%.

7. Triazido[diethylenetriamine]cobalt[III], $[Co[dien][N_3]_3$—21 g. [0.072 mole] cobalt[II] nitrate 6-hydrate, 20.4 g [0.32 mole] sodium azide, 5.8 g [0.144 mole] sodium hydroxide, and 17.4 g [0.29 mole] glacial acetic acid were added in that order to 70 ml water and mixed well. A pink slurry resulted. Aeration of the mixture was started and 6 ml of diethylenetriamine[dien] in 24 ml water was slowly added. The slurry initially took on a dark red color. Aeration was continued for 90 min. while the color of the mixture changed from red to dark green-violet. The mixture was cooled in an ice-water bath and suction-filtered. The recovered solids were washed with small portions of cold water until the washings were pale green. The product was then washed with alcohol, then ether, and air-dried. The yield was 13.5 g [60% based on cobalt nitrate]. The dark purple product dissolves readily in DMSO, less so in acetone to give a green solution. Analysis: found: Co-19.9%, N-58.4%, C-16.9%, H-4.5%, theor.: Co-20.3%, N-58.8%, C-17.0%, H-4.6%.

8. Azidooxalatodiethylenetriaminecobalt[III], $[Co[dien][C_2O_4][N_3]]$—2 g of triazidodiethylenetriaminecobalt[III], was added to 20 ml water and 2 g oxalic acid was stirred in. The mixture was heated on a steam bath for about 20 min. during which a deep purple color developed. The solution was cooled in an ice bath. The purple solid was suction-filtered, washed with about 60 ml alcohol, then ether and air-dried. The yield was *1.5 g.

The filtrate and alcohol washings were combined, cooled in an ice bath after which an additional amount of product was formed and recovered. Analysis: found: Co-20.0%, C-24.3%, H-4.4%, theor.: Co-20.1%, C-24.7%, H-4.45%.

9. Azidodinitrodiethylenetriaminecobalt[III], $[Co[dien][NO_2]_2[N_3]]$—One gram of chlorodinitrodiethylenetriaminecobalt[III]^(15) and 0.5 g sodium azide were added to 10 ml water and heated on a steam bath for 90 min. There was no apparent color change. The mixture was cooled in an ice-water bath, suction-filtered, washed with alcohol, then ether and air-dried. The product was darker in color than the starting material and the infrared spectrum showed the characteristic bands for the coordinated azido group. The yield was 1.0 g. Analysis: found: Co-19.6%, C-16.1%, N-37.6%, H-4.4%, theor.: Co-19.9%, C-16.2%, N-37.8%, H-4.39%.

10. Diazidochlorodiethylenetriaminecobalt[III], $[Co[dien][N_3]_2Cl]$—Two grams of $[Co[dien][N_3]_3]$ were placed under 20 ml 6M HCl for three hours. A brown solid was observed to form. After cooling in an ice bath, the mixture was suction-filtered to give a chocolate brown solid and a purple filtrate. The precipitate was washed with alcohol, ether, and air-dried. The yield was 1.1 g of brown powder. Analysis: found: Co-20.5%, N-44.3%, theor. Co-21.0%, N-45.0%.

C. *Analyses* In addition to elemental analyses, the purity of the preparations was checked by thin layer chromatography on commercially precoated silica gel plates (Type Q-1, Quantum Industries, Fairfield, N.J.), eluting with CH_3OH:DMSO: $HClO_4$ (60 : 40 : 0.1) or acetone. A few samples were checked by paper electrophoresis as previously described (1).

DISCUSSION

In addition to the method outlined above, a number of other procedures were followed for the preparation of triazidotriamminecobalt[III].These included preparations from tris(carbonato)cobaltate[III] ion as well as by varying the temperature of oxidations and speed of evaporation of the solvent in the method cited. As indicated by their identical infrared and PMR spectra, and by thin layer chromatography, all preparations gave the same product which was identified as the *meridional* isomer.

The best evidence for the assignment of the *meridional* structure to this complex was provided by the proton magnetic resonance spectrum as shown in Fig. 1. The areas under the ammine proton peaks at 3.32 and 2.84 delta integrate as approximately 2 : 1 as expected for the *meridional* isomer where two ammines are *trans* to one another while the third is *trans* to an azide ligand. The *facial* complex would be expected to show only one resonance as all ammines are opposite an azide ligand.

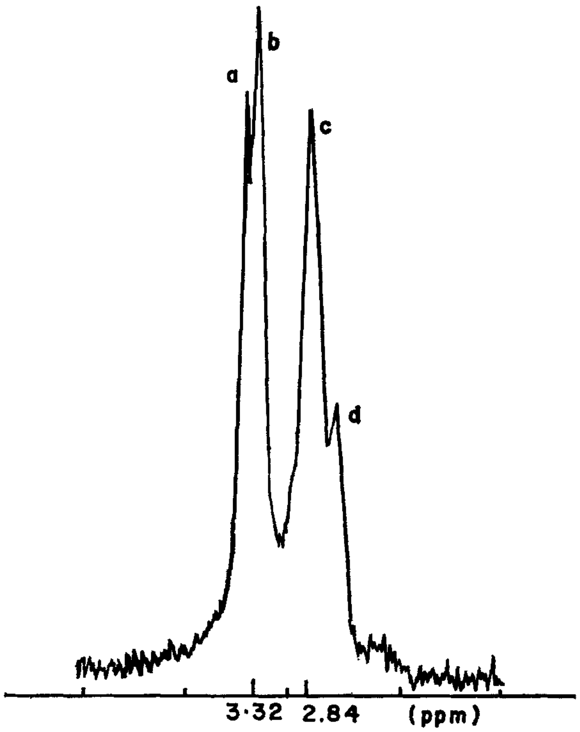


FIGURE 1 PMR Spectrum of $(Co(NH_3)_3(N_3)_3)$

a. water impurity
b. NH_3 protons from 1,6 positions
c. NH_3 protons from 2 position
d. DMSO peak.

In the course of running the PMR spectra, it was noticed that the $(Co(NH_3)_3(N_3)_3)$ was quite sensitive to water after prolonged periods of time. A new resonance peak can be seen at 3.82 delta corresponding to coordinated water which may have replaced an azide group in the complex. The solvolyses reaction can also be observed by thin layer chromatography of this solution. Unreacted $[Co[NH_3]_3[N_3]_3]$ has $R_f = 0.99$ using a solution of only acetone, while a new spot appears at $R_f = 0.55$ which could correspond to a complex with a +1 charge such as the $[Co[NH_3]_3[H_2O][N_3]_2^+$.

Table I tabulates the PMR spectra for a number of azidoaminecobalt[III] complexes and includes, for comparison, values previously obtained(1) for both isomers of $[Co[NH_3]_3[NO_2]_3]$ as well as for *mer*-$[Co[NH_3]_3[NCS]_3]$. The characteristic of all of these *meridional*-triammines is that the proton resonances form the ammines *trans* to one another are downfield from those of the ammine *trans* to an acido ligand.

The PMR spectrum of $[Co[NH_3]_3[N_3]_3]$ was easy to interpret when compared to that of $[Co[dien][N_3]_3]$ [dien = diethylenetriamine or 1,4,7-triazaheptane]. The ammine protons of the diethylenetriamine would be expected to show at least two peaks, corresponding to the primary and secondary amines, whether in the *facial* or *meridional* arrangement. The PMR spectrum of this complex is shown in Fig. 3. One of the most obvious features is that now the smaller peak at 5.65 is the downfield peak. The resonance form the protons of the terminal amines is split into two peaks at 4.46 and 4.30 each approximately twice the size of the 5.65 resonance. This splitting of the ammine proton peaks is similar to that encountered in *cis*-$[Co[en]_2[N_3]_2]^+$ [see table 1] and *cis*-$[Co[en]_2[NO_2]_2]^+$(16) and is attributed in these isomers to those ammines *trans* to an acido ligand where one proton on each nitrogen is directed towards the ethylenic protons while the other is directed towards the anionic ligand.

The assignment of the *meridional* configuration to this complex is based on the resonances observed for the ethylenic proton of the amine. Basicly, there are two kinds: those adjacent to a secondary amine [at the 3,5-positions] and those adjacent to a primary amine [at the 2,6-positions]. For the *facial* isomer, *each* of these resonances should be further split because one proton on each carbon is directed towards the azide group while the other is directed towards the ethylenic and amine protons. For the *meridional* isomer, the protons at the 2,5-positions of the amine are both directed away from the complex and while these might be in slightly different environments, any splitting of the peaks would be small and could not be detected in our solutions. The spectrum shown, in spite of the interference from the DMSO, clearly shows three peaks with the one at 2.78 clearly larger than the two roughly equal sized peaks at 2.63 and 2.30.

TABLE I

Proton Magnetic Resonance Spectra

COMPLEX	delta	REL.INTENS.	IDENTITY
mer-Co(NH$_3$)$_3$(N$_3$)$_3$	2.84	1	NH$_3$ trans to N$_3$
	3.32	2	NH$_3$ trans to NH$_3$
mer-Co(NH$_3$)$_3$ (NCS)$_3$	3.35	1	NH$_3$ trans to NCS (Ref. 19)
	3.92	2	NH$_3$ trans to NH$_3$
mer-Co(NH$_3$)$_3$(NO$_2$)$_3$	2.96	1	NH$_3$ trans to NO$_2$ (Ref. 1)
	3.34	2	NH$_3$ trans to NH$_3$
fac-Co(NH$_3$)$_3$(NO$_2$)$_3$	3.35		all NH$_3$ trans to NO$_2$
mer-Co(dien)(N$_3$)$_3$	2.30	2	CH$_2$ at 2,6-positions
	2.63	2	
	2.78	4	CH$_2$ at 3,5-positions
	4.30	2	NH$_2$ at 1,7-positions
	4.46	2	
	5.65	1	NH at 4-position
mer-Co(dien)(C$_2$O$_4$)(N$_3$)	2.4	4	CH$_2$ at 2,6-positions
Note (*a*)	2.6	4	CH$_2$ at 3,5-positions
	3.5	4	NH$_2$ at 1,7-positions
	4.6	1	NH at 4-position
Co(dien)(NO$_2$)$_2$(N$_3$)	—		
Note (*a*)	2.9		CH$_2$ at 3,5-positions
	4.2		NH$_2$ at 1,7-positions
cis[-Co(en)$_2$(N$_3$)$_2$]·N$_3$	3.88	1	NH$_2$ trans to N$_3$
Note (*b*)	4.16	1	
	4.85	1	NH$_2$ trans to NH$_2$
	5.16	1	
trans[-Co(en)$_2$(N$_3$)$_2$]·N$_3$	2.60	1	CH$_2$ protons (all)
	4.65	1	NH$_2$ trans to NH$_2$

Ref. 19: L. F. Druding and H. C. Wang, unpublished research.

Note (*a*): Concentration of complex was to low to see proton positions clearly. Solvent band obscured CH$_2$ peaks as well as hindered exact ratio elucidation.

Note (*b*): Solvent band obscured CH$_2$ peaks of ethylenediamine.

As additional evidence that the diethylenetriamine adopted the *meridional* structure, oxalate was substituted for two azides under conditions where it was assumed that no rearrangement of the amine took place. The possible geometric isomers of the product, azidooxalatodiethylenetriaminecobalt[III] are shown in Fig. 4. The PMR spectrum of I for *fac*-dien should show three amine proton resonances with a ratio of 2 : 2 : 1 corresponding to the terminal amines [-NH$_2$] *trans* to an azide and an oxalate oxygen and the middle amine [-NH-] *trans* to an oxalate oxygen. Structure II for *fac*-dien and structure III for *mer*-dien would both be expected to show two amine proton peaks in a 4 : 1 ratio as both structures have terminal amines *trans* to identical ligands (this ignores fine structure for semi axial vs. equatorial protons on the terminal amines). Experimentally two peaks were found with the 4 : 1 ratio. Both peaks were quite symmetric which strongly suggests the *meridional* arrangement for the amine. This assumption is based on the PMR spectra of diazidobis[ethylenediamine]cobalt[III] complexes. These spectra are similar to those observed for the dinitro complexes(16) where the *trans*-dinitro complex has but a single amine proton resonance while the

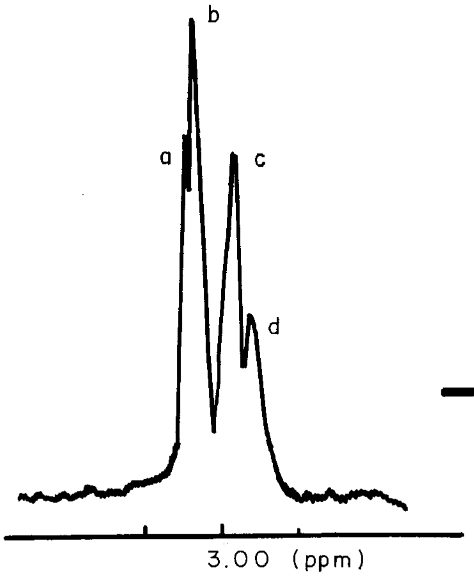


FIGURE 2a PMR spectra of *mer*-(Co(NH_3)$_3$(N_3)$_3$)
a. H_2O peak
b. NH_3 protons for the 1,6 positions
c. NH_3 protons for the 2 position
d. DMSO protons

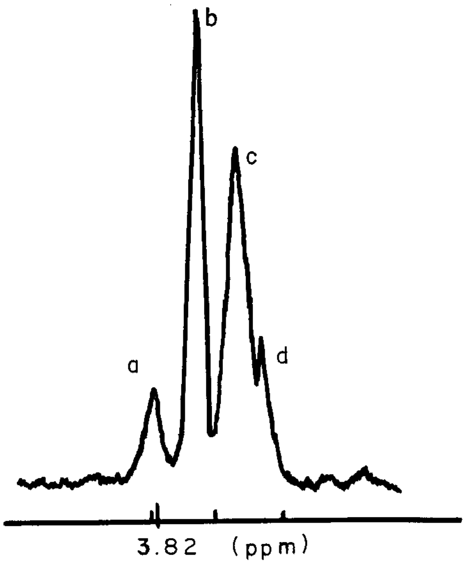


FIGURE 2b PMR spectra of the aquation product of CO(NH_3)$_3$(N_3)$_3$
a. Coordinated H_2O
b. NH_3 protons from the 1,6 positions
c. NH_3 protons for the 2 position
d. DMSO protons

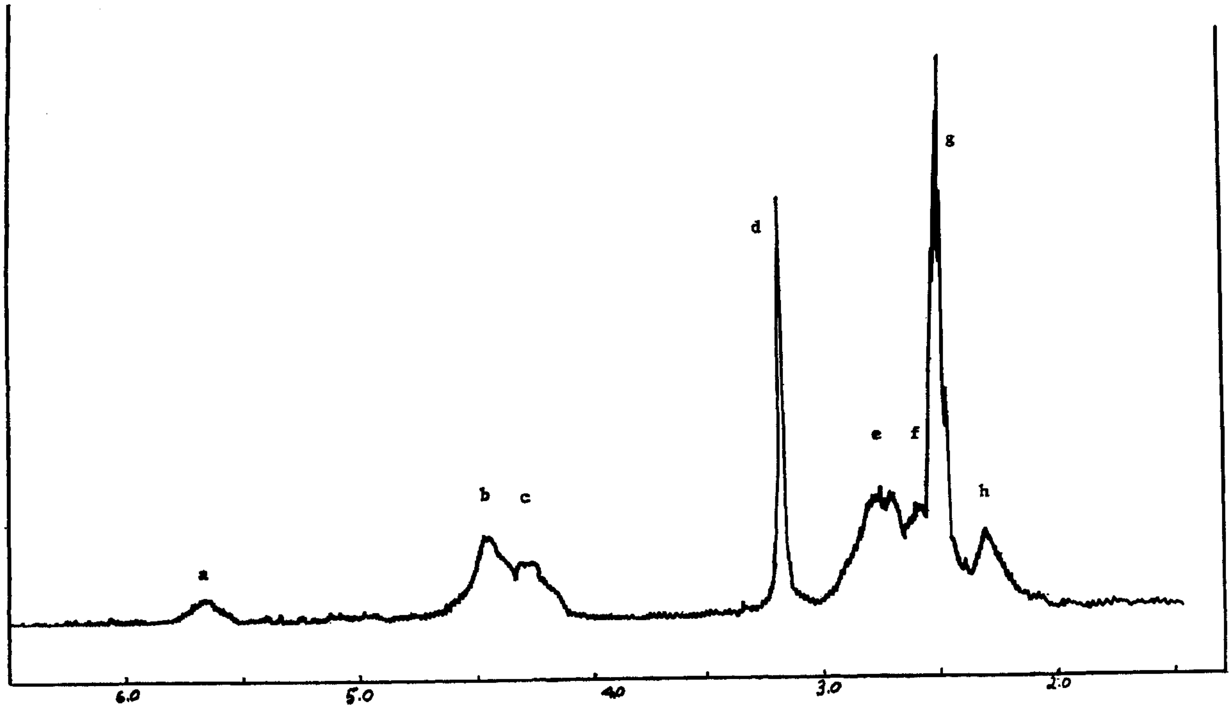
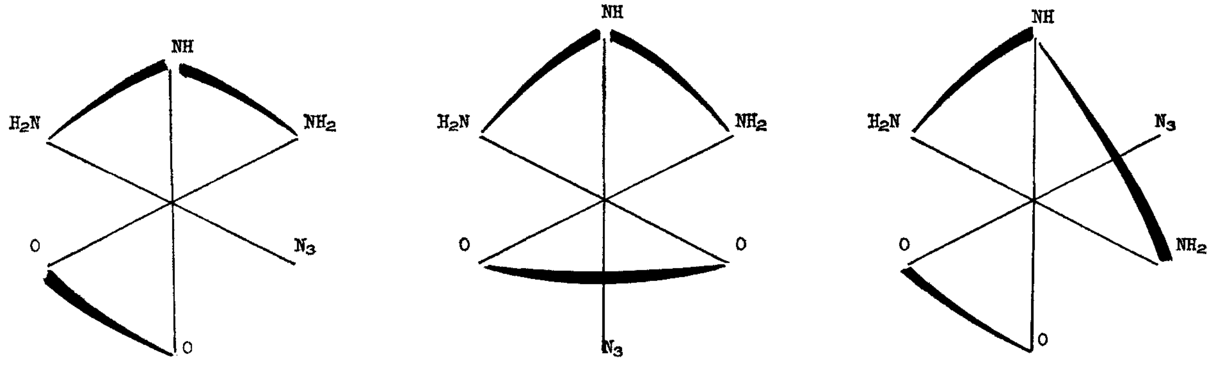


FIGURE 3 PMR Spectra of *mer*-[Co[dien][N_3]$_3$]

a. NH proton resonance
b,c. Water impurity
e. CH_2 proton resonance from 3,5-position
f,h. CH_2 proton resonances from 2,6-positions
g. DMSO resonances



I II III

FIGURE 4 Geometrical Isomers of [Co[dien][C_2O_4][N_3]]

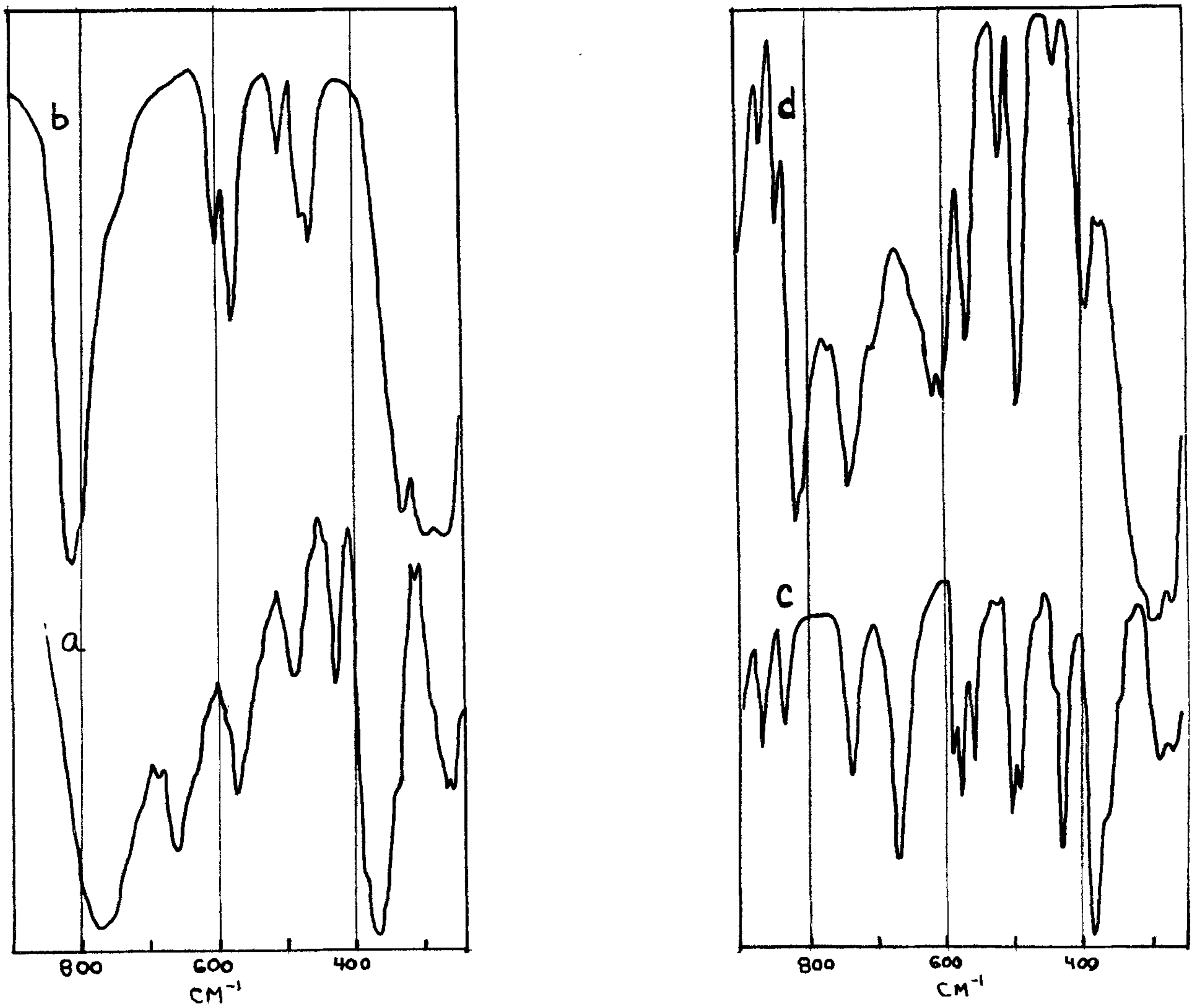


FIGURE 5 Infrared Spectra of Some Triamines

a. *mer*-[Co[NH_3]$_3$[N_3]$_3$] *b*. *mer*-[Co[NH_3]$_3$[NO_2]$_3$] *c*. mer-[Co[dien][N_3]$_3$] *d*. mer-[Co[dien][NO_2]$_3$]

cis-dinitro complex has three peaks due to a splitting of the protons of the amines *trans* to the anionic ligand caused by one proton being directed towards the ligand while the other is directed towards the ethylenic chain. Since the resonance peak of the terminal amine protons observed for $[Co[dien][C_2O_4]N_3]]$ is a single symmetric peak, it was assumed that the diethylenetriamine has adopted the *meridional* configuration in this complex. The solvent peak in this sample was too strong to examine the fine structure of the ethylenic protons.

As previously noted with the isomers of trinitrotriamminecobalt(III), the infrared spectra are not as reliable as indicators of the geometry of the complexes because both isomers are sufficiently asymmetric to produce complex spectra. Recently, Legg and Schneller(17) have suggested that assignment of configuration of the triaminecobalt(III) complexes can be aided by examination of the infrared absorptions of the $Co–N[NH_3]$ and $Co–N[N_3]$ vibrational modes. The *facial* configuration should show two modes each while the less symmetrical *meridional* isomer should show three modes each.

In Fig. 5, the infrared spectra of $[Co[NH_3]_3[N_3]_3]$ and $[Co[dien][N_3]_3]$ are compared with those of the corresponding *mer*-trinitro complexes in the region

TABLE II

Summary of Infrared Spectra: Azide Absorption Frequencies

Complex	V_2 [asym. stretch]	V_1 [sym. stretch]	V_2 [def.]	$Co-N[N_3]$
$[Co[NH_3]_5[N_3]][ClO_4]_2$	2045 cm^{-1}	1315 cm^{-1}	616 cm^{-1}	
$[Co[NH_3]_5[N_3]]Cl_2$	2048		650	
$[Co[NH_3]_5[N_3]][N_3]_2$	2040	1308	630, 610	380 cm^{-1}
cis-$[Co[NH_3]_4[N_3]_2]N_3$	2040, 2130	1290	637	388, 360sh
cis-$[Co[en]_2[N_3]_2]N_3$	2030	1325	660	401, 380
cis-$[Co[en]_2[N_3]_2]Br^a$			657, 677	
cis-$[Co[en]_2[N_3]_2]ClO_4{}^a$	2028, 2075			
trans-$[Co[NH_3]_4[N_3]_2]N_3$	2020	1388, 1295	640	380
trans-$[Co[en]_2[N_3]_2]N_3$	2010	1285	633	385
trans-$[Co[en]_2[N_3]_2]I^a$			667, 677	
trans-$[Co[en]_2[N_3]_2]ClO_4{}^a$	2020			
mer-$[Co[NH_3]_3[N_3]_3]$	2010, 1985	1260, 1300sh, 1335	675	377, 348sh, 395sh
mer-$[Co[dien][N_3]_3]$	2055, 1995, 1963	1320, 1291sh	672	383, 368sh, 348sh
mer-$[Co[NH_3]_3[C_2O_4][N_3]]$	2042	1265, 1300	572, 663	400, 380sh
mer-$[Co[dien][C_2O_4][N_3]]$	2041	1267, 1305	675	390, 375, 356
mer-$[Co[NH_3]_3[NO_2]_2[N_3]]$	2045	1300, 1280, 1260	630	380, 350sh
mer-$[Co[dien][NO_2]_2[N_3]]^c$	2010	1252, 1295	670	375
mer-$[Co[dien][N_3]Cl]$	2140, 2025	1245		
$[Co[N_3]_4]^{2-\,b}$	2089, 2050	1338, 1280	642, 610	
KN_3	2115, 2040sh		632	

[a] Ref. 8, P. J. Staples and M. L. Tobe, *J. Chem. Soc.* **1960,** 4812

[b] Ref. 10, D. Forster and W. D. Horrocks, *Inorg. Chem.* **5,** 1510 [1966].

[c] NO_2 bending at 815, 835 cm.$^{-1}$

300–800 cm^{-1}. The Co–N[N_3] stretching mode for [Co[NH_3]$_3$[N_3]$_3$] appears at 377 cm^{-1} with shoulder at 395 and 348 cm^{-1}. Likewise the complex, [Co[dien][N_3]$_3$] has its band at 383 cm^{-1} with shoulders at 368 and 348 cm^{-1}. The Co–N[NH_3] bands appear at 495 and 436 cm^{-1} with a shoulder at 450 cm^{-1} for the triamine. The spectra of [Co[dien][N_3]$_3$] and [Co[dien][N_3]$_3$] show the same pattern of peaks in the region of 500–600 cm^{-1} for the Co–N[NH_3] stretching. A more complex spectrum is expected for the diethylenetriamine complexes because its symmetry is considerably less than the C_{2v} assumed for *mer*-[Co[NH_3]$_3$[N_3]$_3$].

Staples and Tobe(8) also observed a splitting in the asymmetric azide frequency of *cis*-[Co[en]$_2$[N_3]$_2$]$^+$ but not for the *trans* isomer. This was confirmed in this work as well as for similar behavior by the *cis* and *trans* [Co[NH_3]$_4$[N_3]$_2$]$^+$ complexes. Both triazido complexes should show this splitting because of *cis*-azides. In [Co[NH_3]$_3$[N_3]$_3$], these bands appear at 1985 and 2010 cm^{-1} while for [Co[dien][N_3]$_3$] they appear at 1963, 1995 and 2055 cm^{-1}. In both triazido complexes, the strongest absorption was the highest energy peak instead of being equal in strength as in the *cis*-diazido complexes, which suggests that there are two different kinds of azide positions in the complex as would be true for the *meridional* isomer but not for the *facial* one.

The asymmetric azide stretching band in [Co[dien][N_3]$_2$Cl] is also split, suggesting that for the *meridional* configuration of the amine, then the azides are *cis* to one another.

In [Co[NH_3]$_3$[NO_2]$_2$[N_3]] and [Co[dien][NO_2]$_2$[N_3]], assuming retention of the *meridional*-amine configuration, the nitro groups are most probably *cis* to one another by virtue of the splitting of the NO_2 bending mode at 800 cm^{-1} (18) The azidodinitro complexes were prepared from the chlorodinitro complexes which in turn were prepared from the reaction of HCl on the *meridional*-trinitro complexes. If the *trans*-labilizing effects are functioning in this octahedral system, then the nitro group, being a better *trans*-labilizing group than the amine directs the nitro *trans* to a nitro replacement, leaving finally a *cis*-dinitro arrangement. This is also consistent with the formation of [Co[dien][N_3]$_2$Cl] where *cis* azido groups remain after an azide is replaced by chloride, and azide is known to be a better *trans* labilizing group.

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REFERENCES

1. R. B. Hagel and L. F. Druding, *Inorg. Chem.* **9,** 1496 (1970).
2. F. R. Keene, G. H. Searle, Y. Yoshikawa, A. Imai, K. Yamasaki, *Chem. Commun.* **1970,** 784.
3. S. H. Caldwell and D. A. House, *J. Inorg. Nucl. Chem.* **31,** 811 (1969).
4. M. Linhard and M. Weigel, *Z. anorg. Chem.* **263,** 245 (1950).
5. A. R. Gainsford and D. A. House, *J. Inorg. Nucl. Chem.* **32,** 688 (1970).
6. N. F. Curtis, R. W. Hay and Y. M. Curtis, *J. Chem. Soc.* (A), **1968,** 182.
7. K. Nakamoto, *Infrared Spectra of Inorganic and Coordination Compounds*, 2nd Ed., Wiley-Interscience, New York, 1970.
8. P. J. Staples and M. L. Tobe, *J. Chem. Soc.* **1960,** 4812.
9. P. J. Staples, *J. Chem. Soc.* **1963,** 138.
10. D. Forster and W. D. Horrocks, *Inorg. Chem.* **5,** 1510 (1966).
11. H. H. Schmidtke and D. Garthoff, *J. Am. Chem. Soc.* **89,** 1317 (1966).
12. W. Beck, W. F. Fehlhammer, P. Pollman, E. Schuierer and K. Fedl, *Chem. Ber.* **100,** 2335 (1967).
13. M. Linhard and H. Flygare, *Z. anorg. Chem.* **262,** 328 (1950).
14. G. S. Schlessinger, *Inorganic Laboratory Preparations*, Chemical Publishing Co., N.Y. 1962.
15. P. N. Crayton, *Inorg. Syn.* **7,** 207 (1963).
16. T. E. MacDermott, *Inorg. Nucl. Chem. Lett.* **5,** 463 (1969).
17. J. I. Legg and M. C. Schneller, Abstracts of 26th Northwest Regional Meeting, American Chemical Society, Seattle, Wash., 1971.
18. J. Chatt, L. A. Duncannon, B. M. Gatehouse, J. Lewis, R. S. Nyholm, M. L. Tobe, P. F. Todd and L. M. Venanzi, *J. Chem. Soc.* **1959,** 4073.