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Triammines of Cobalt(III). IV. Preparation, Properties, and Structure of the Polymerization Isomer *trans*-Diazidotetraamminecobalt(III) *trans*-Tetraazidodiamminecobaltate(III), $[Co(NH_3)_4(N_3)_2][Co(NH_3)_2(N_3)_4]$

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The crystal and molecular structure of *trans*-diazidotetraamminecobalt(III) *trans*-tetraazidodiamminecobaltate(III) was determined by three-dimensional X-ray analysis using Ni-filtered Cu Kα radiation. The compound was found to be triclinic of space group $P\bar{1}$ with pertinent unit cell data: $a = 7.661$ (6) Å, $b = 6.928$ (6) Å, $c = 9.671$ (8) Å, $\alpha = 87.4$ (6)°, $\beta = 72.7$ (6)°, $\gamma = 116.4$ (7)°, $Z = 1$, $d_{obsd} = 1.87$ (2) g cm^{-3}, $d_{calcd} = 1.867$ g cm^{-3}. The structure was solved by normal Patterson and Fourier methods and refined by full-matrix least-squares analysis to a final discrepancy factor ($R = [\sum||F_o| - |F_c||]/\sum|F_o|$) of 0.049 for 583 observed reflections ($I > 2.5\sigma_I$). Infrared and NMR spectroscopy of this compound is reported with emphasis on the previously unknown anionic tetraazido moiety. Each cobalt atom, located on a special position, is coordinated by six nitrogen atoms in an octahedral configuration. The maximum distortion of the octahedron is 4.4 (6)° from the expected 90° angle. The unique azide of the diazido moiety exhibits a N–N–N bond angle of 172.5 (12)°. The average Co–NH_3 bond length is 1.98 Å and the Co–N_3 average bond length is 1.97 Å. Extensive intermolecular hydrogen bonding is present, between the bonding nitrogen of an azide and a neighboring ammine hydrogen atom.

Introduction

Introductions to the type of isomerization demonstrated by inorganic coordination complexes include polymerization isomers, where the actual molecular compositions are multiples of the simplest stoichiometric placement of atoms about the metal center. Within a system recently investigated in this laboratory, trinitrotriamminecobalt(III)[1] has known polymerization isomers: $[Co(NH_3)_6][Co(NO_2)_6]$[2] and $[Co(NH_3)_4(NO_2)_2][Co(NH_3)_2(NO_2)_4]$.[3] There are sizable differences in chemical and physical properties in these isomers resulting from differences in arrangement of ligands about the metal center.[4]

In a previous chemical and spectroscopic examination of triazidotriamminecobalt(III),[5] the meridional isomer was the easiest formed, yet in several preparations, varying reaction conditions, a darker crystalline material of an extremely unstable nature was produced. A small amount of the black material was mechanically separated for spectroscopic and crystallographic identification. The proton magnetic resonance spectrum revealed a single broad peak suggesting the possible existence of a facial isomer consistent with a molecular weight calculated for this complex. Therefore a crystal of suitable quality was selected for X-ray crystallographic study. This study resulted in the identification of this material as a cobalt(III) polymerization isomer.[6]

While few anionic azido coordination complexes are known for other metals,[7] none contain mixed ligands, and no other anionic complexes have been reported for cobalt(III) with an azide group.

Experimental Section

Preparation of *trans*-Diazidotetraamminecobalt(III) *trans*-Tetraazidodiamminecobaltate(III). To a solution of 1.0 g of $CoSO_4 \cdot 7H_2O$ and 0.5 g of ammonium sulfate in 10 ml of water and 6.0 ml of 20% aqueous ammonia was added 1.4 g of sodium azide. The mixture was aerated for 2.5 hr and slowly evaporated to about one-eighth of its original volume, on a steam bath. *Warning*! Do not allow to evaporate to dryness; this is a dangerous detonator. Filtration of the mixture will produce a good yield of crystals which are largely the polymerization isomer. Microscopic investigation reveals them to be short, thin rods, with many crystals twinned, an observation noted for other cobalt–azido complexes.[8] The isomer could not be recrystallized without decomposition, presumably because of loss of an azide group from the anion. Anal. Calcd: Co, 24.9; N, 71.2. Found: Co, 24.6; N, 69.0 (fast decomposition resulted in loss of some nitrogen).

Spectroscopy. The infrared spectrum of $[Co(NH_3)_4(N_3)_2][Co(NH_3)_2(N_3)_4]$ was determined with a Beckman Model IR-10 spectrophotometer using KBr disks and Nujol mulls. This compound, in spite of its instability, could be compressed to 12,000 psi in KBr without apparent decomposition. Both modes of sample preparation gave identical infrared spectra, which are presented in Figure 1.

Proton magnetic resonance spectra were recorded with Varian A-60 and Varian XL-100 instruments at 60 and 100 MHz, respectively. All samples were dissolved in DMSO-d_6 with a concentration of ca. 5% by weight and run against internal TMS. PMR spectra are presented in Figure 2.

Polarography. A Princeton Applied Research Electrochemistry System, Model 170, was employed to collect the direct current polarograms. An H cell with anode and cathode separated by a porous glass frit was used. A PAR controlled-rate dropping mercury electrode was used, and best results were obtained with a drop time of 0.5 sec. The usual procedures of deaeration with nitrogen and use of Triton X-100 as a maximum suppressor were followed.

Solutions ranging in concentration from 10^{-3} to 10^{-4} *N* were carefully prepared by weighing samples on a microbalance and dissolving in 0.1 *N* KNO_3. These concentrations were found to give the best results, as well as being safer to handle in terms of sample size.

The polarograms were determined at 25.00 ± 0.25° in a thermostated cell, and the analyses were run immediately after preparation. There was no observable change in pH during electrolysis; therefore buffering proved unnecessary. On long standing, however, there was considerable change in pH, presumably as a result of hydrolysis of the azide ligand followed by oxidation.[9] The azide diffusion currents were analyzed (Figure 3) according to the procedures described by Bryant and Kemp.[10]

X-Ray Data Collection and Reduction. The compound was prepared as cited above. It is unstable and could not be recrystallized without decomposition. A suitable chip of a crystal measuring 0.09 × 0.03 × 0.03 mm was chosen from the preparative mixture and mounted with quick-drying epoxy resin (the *a* axis paralleling the glass tube) in a capillary with an atmosphere of other crystals of this complex, placed at the bottom of the sealed tube. Weissenberg photographs indicated a triclinic space group with no apparent systematic absences, although the $k + 1 =$ odd reflections were considerably weaker than the $k + 1 =$ even data (indicating the existence of atoms located on a special position). The space group assignment was made on this basis as space group $P1$ or $P\bar{1}$. The unit cell parameters used in data collection[11] are $a = 7.661$ (6) Å, $b = 6.928$ (6) Å, $c = 9.671$ (8) Å, $\alpha = 87.4$ (6)°, $\beta = 72.7$ (6)°, $\gamma = 116.4$ (7)°, and $V = 429.4$ Å^3. The cell constants were obtained by a least-squares fit of 15 reflections using Ni-filtered Cu Kα radiation (λ 1.54051 Å) and a Hilger and Watts Model Y.290 diffractometer equipped with a PDP-8 computer and four full circles. A measured density of 1.87 (2) g cm^{-3} was obtained by flotation of several crystals in 1,2-dibromomethane–CCl_4.

The Hilger and Watts diffractometer was used to collect data at room temperature (22 ± 1°). Cu Kα radiation (λ 1.54051 Å) with a Ni filter was used for data collection (Mo radiation was not

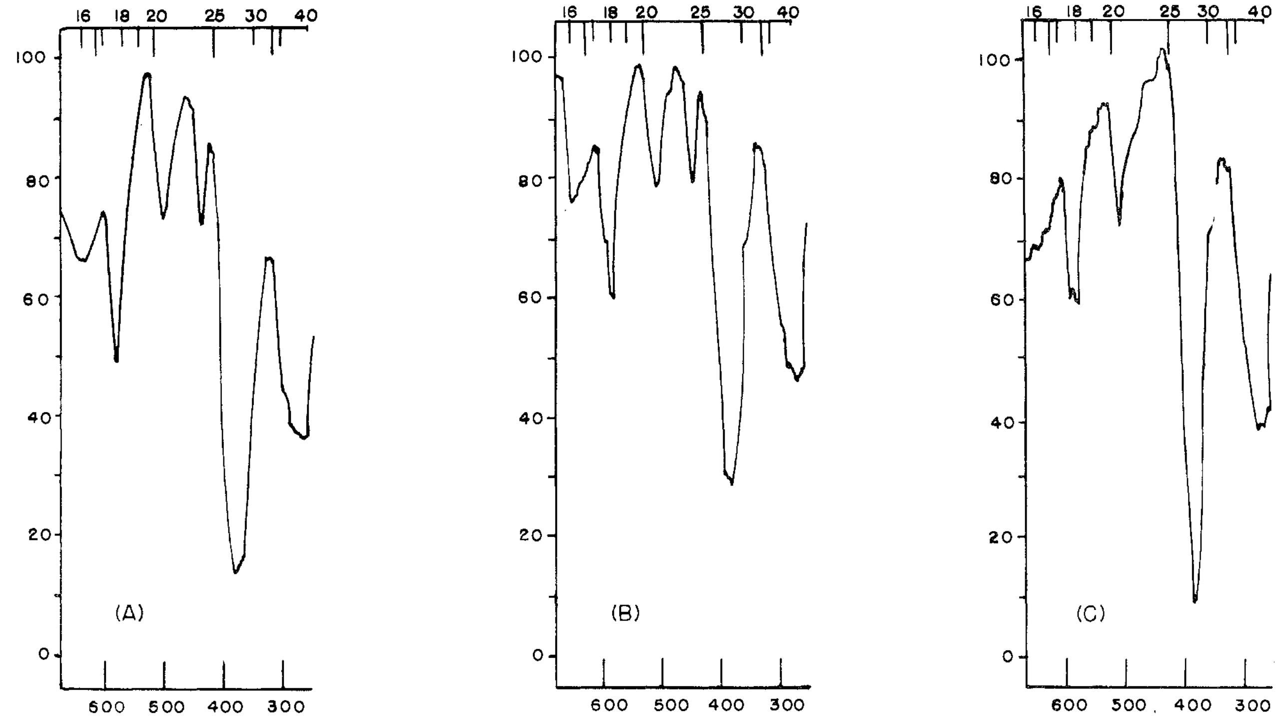

Figure 1. Ir spectra of (A) *mer*-$Co(NH_3)_3(N_3)_3$, (B) [*trans*-$Co(NH_3)_4(N_3)_2$][*trans*-$Co(NH_3)_2(N_3)_4$], and (C) [$Co(NH_3)_4(N_3)_2$]·Cl.

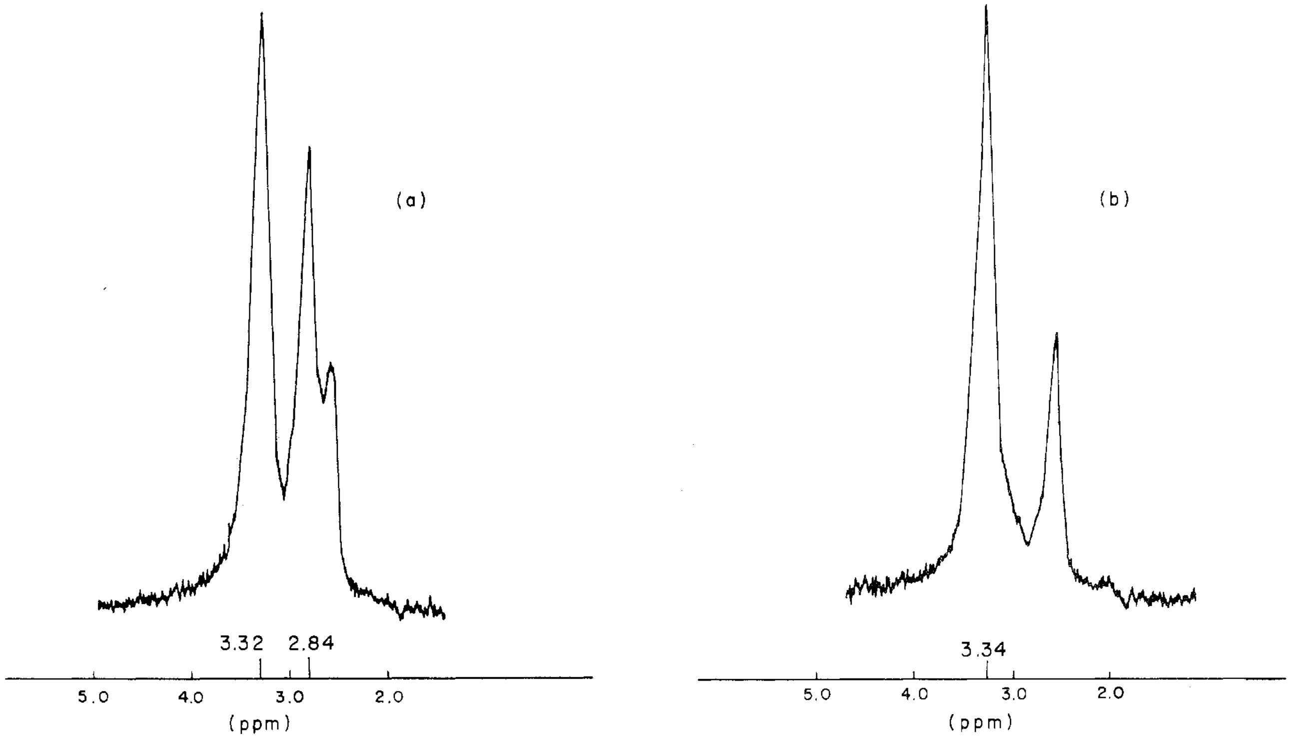

Figure 2. PMR spectra, 100 MHz, of (a) *mer*-$Co(NH_3)_3(N_3)_3$ and (b) [*trans*-$Co(NH_3)_4(N_3)_2$][*trans*-$Co(NH_3)_2(N_3)_4$].

available); diffracted radiation was detected by a scintillation counter and a pulse height discriminator. A unique set of data was collected to a θ maximum of 72° by a 2θ–θ scan technique. A scan range of 1.0° was used with 50 steps being measured at a scan rate of 2 sec/step. A background measurement was made at the start and finish of each scan procedure equal to half the total scan time. There were four standard reflections measured every 100 to detect the extent of crystal decomposition or movement (scale factors were calculated from the relative intensity of the standards and indicated some decomposition, maximum of 10%; if the intensity drop was greater than 10%, the instrument was programmed to recenter a number of reflections and to recalculate the orientation matrix). Attenuation of the X-ray beam was not necessary since the maximum observed count rate was within the linear range of the counter. A total of 1208 reflections were recorded of which 583 were judged to be significantly ($2.5\sigma_I$) greater than background {σ_I = [total scan count + sum of BG counts/(BG to scan ratio)^2]$^{1/2}$ × scan rate}.

Lorentz and polarization corrections were calculated and applied to all data. Absorption corrections were applied by the method of Coppens et al.[12] The grids used for absorption correction evaluation were 4 × 4 × 4, 4 × 4 × 10, and 8 × 8 × 20. No significant differences of transmission coefficients were calculated between any of these grid sizes. Therefore, the 4 × 4 × 4 grid (parallel to *a*, *b*, and *c*) was used to correct the entire data set. Calculated transmission coefficients were in the range of 0.44–0.28.

Solution and Refinement of the Structure. The structure was solved

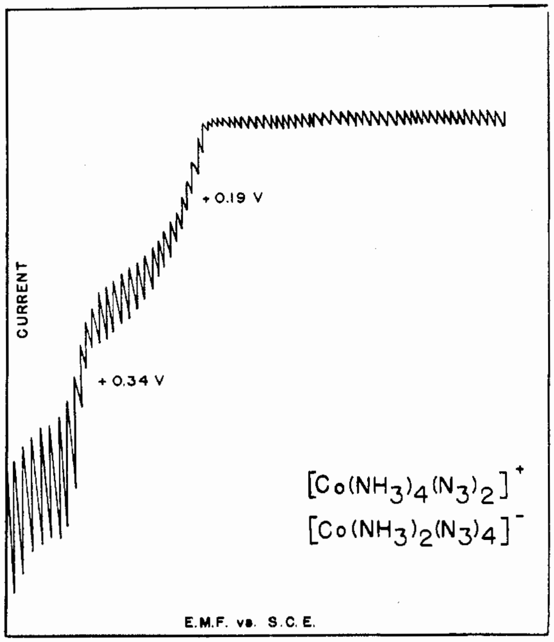

Figure 3. Polarogram of *trans*-diazidotetraamminecobalt(III) *trans*-tetraazidodiamminecobaltate(III). Note the distinct difference in the emf of each moiety of the complex.

Table I. Final Atomic Positions[a]

	x	y	z
Co	0.0	0.0	0.0
N1	0.1529 (17)	0.3166 (14)	0.9143 (9)
N2	0.2277 (17)	0.4469 (14)	0.9833 (9)
N3	0.3039 (21)	0.5781 (15)	0.0459 (8)
N4	0.0621 (15)	0.9394 (9)	0.7982 (6)
N5	0.1999 (12)	0.0867 (12)	0.6986 (7)
N6	0.3349 (10)	0.2241 (15)	0.5991 (8)
N7	0.2553 (13)	0.0065 (10)	0.0132 (7)
Co′	0.0	0.5	0.5
N8	0.1231 (15)	0.7998 (12)	0.3852 (9)
N9	0.3065 (15)	0.9278 (13)	0.3365 (9)
N10	0.4743 (17)	0.0640 (15)	0.2836 (11)
N11	−0.1668 (13)	0.3992 (11)	0.3719 (7)
N12	0.2173 (14)	0.4382 (13)	0.3730 (7)

[a] Standard deviations appear in parentheses.

using a normal Patterson calculation and the usual Fourier analyses. Space group $P\bar{1}$ was chosen for structure solution (a statistical analysis of the data was made after the structure was refined and confirmed the centricity of this system). $P\bar{1}$ has two special positions, and the presence of one molecule suggests the positions of the heavy atoms are at coordinates 0, 0, 0 and 0, $^1/_2$, $^1/_2$. A Fourier calculation based on these parameters revealed several areas of high electron density about each cobalt atom at reasonable distances and angles, forming two superimposed octahedra, making structure choice difficult. After several attempts, all nonhydrogen atoms were resolved with resulting R factors of $R_1 = 0.23$ and $R_2 = 0.25$ where

$$R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$$

$$R_2 = [\Sigma w||F_o| - |F_c||^2/\Sigma w|F_o|^2]^{1/2}$$

The structure was refined by full-matrix least squares minimizing the function R_2, where w is a modified Cruickshank weight

$$w = 1.0/(A + F_o + BF_o)^2$$

$$A = 2F_{\text{min}}$$

$$B = 2/F_{\text{max}}$$

Table II. Final Anisotropic Thermal Parameters ($\times 10^4$)[a]

	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Co	185 (11)	140 (6)	68 (2)	33 (6)	33 (4)	7 (3)
N1	341 (47)	198 (23)	103 (10)	64 (26)	70 (18)	19 (13)
N2	284 (24)	197 (23)	92 (10)	87 (27)	3 (18)	22 (13)
N3	506 (57)	223 (27)	134 (13)	99 (31)	99 (23)	29 (15)
N4	238 (38)	172 (22)	95 (10)	42 (20)	15 (17)	1 (12)
N5	241 (37)	238 (24)	98 (10)	110 (24)	37 (17)	6 (14)
N6	290 (45)	291 (29)	107 (11)	97 (27)	30 (18)	54 (15)
N7	133 (35)	229 (23)	118 (11)	38 (22)	74 (16)	11 (12)
Co′	173 (11)	186 (7)	89 (3)	57 (6)	31 (4)	5 (3)
N8	123 (18)	269 (30)	222 (19)	21 (27)	75 (23)	55 (19)
N9	246 (44)	242 (28)	98 (11)	98 (29)	42 (20)	1 (14)
N10	266 (45)	317 (33)	169 (15)	13 (30)	31 (22)	47 (18)
N11	224 (40)	214 (22)	120 (11)	82 (23)	72 (18)	22 (12)
N12	278 (41)	335 (29)	95 (10)	157 (27)	54 (18)	15 (14)

[a] Standard deviations appear in parentheses. The anisotropic temperature has the form $\exp[-(h^2B_{11} + k^2B_{22} + l^2B_{33} + 2hkB_{12} + 2hlB_{13} + 2klB_{23})]$.

Table III

a. Bond Lengths and Angles[a]

Atoms			Angle, deg	Bond distances, Å	
A	B	C	A–B–C	A–B	B–C
N1	Co	N4	90.4 (3)	1.966 (9)	1.977 (8)
N1	Co	N7	91.0 (4)	1.966 (9)	1.978 (8)
N4	Co	N7	91.6 (3)	1.977 (8)	1.978 (8)
N8	Co′	N11	92.7 (4)	1.965 (9)	1.971 (9)
N8	Co′	N12	94.4 (4)	1.965 (9)	1.981 (9)
N11	Co′	N12	91.7 (4)	1.971 (9)	1.981 (9)
Co	N1	N2	120.8 (7)	1.966 (9)	1.189 (12)
Co	N4	N5	118.1 (7)	1.977 (8)	1.196 (12)
Co′	N8	N9	124.5 (9)	1.965 (9)	1.201 (13)
N1	N2	N3	177.7 (9)	1.189 (12)	1.150 (13)
N4	N5	N6	177.5 (9)	1.196 (12)	1.162 (13)
N8	N9	N10	172.5 (12)	1.201 (13)	1.136 (12)

b. Hydrogen-Bonding Distances (N–N)

Atoms	Distance, Å	Atoms	Distance, Å
N1- - -N11	3.27	N6- - -N12	3.14
N3- - -N12	3.05	N8- - -N7	3.48
N3- - -N7	3.16	N9- - -N7	3.32
N4- - -N11	3.18	N10- - -N7	3.20

[a] Standard deviations appear in parentheses.

The unobserved reflections were assigned zero weights. Initially refinement was made in the isotropic mode for all nonhydrogen atoms and changed to anisotropic when convergence was attained. A difference Fourier revealed the positions of significant electron density in regions where hydrogen atoms of the ammine groups would be expected; inclusion of hydrogen atoms at calculated positions and several cycles of full-matrix least squares reduced the discrepancy index, R_1 to 0.049 and R_2 to 0.061. A final difference synthesis showed no significant features. A list of observed and calculated structure factors is available upon request.[13] Atomic and thermal parameters appear in Tables I and II. Table III presents the bond lengths and angles, including the suspected hydrogen-bond distances.

Atomic scattering factors for all atoms were taken from Cromer and Waber.[14] The real and anomalous contributions to the scattering atom were obtained from ref 15. The least-squares programs used in the analysis were a local modification of those of Busing and Levy[16] while the weighting scheme is that of Cruickshank.[17] Use was also made of a modification of the X-ray 73 system[18] and programs of Blount.[19]

Results and Discussion

The polymerization isomer $[Co(NH_3)_4(N_3)_2][Co(NH_3)_2(N_3)_4]$ consists of two six-coordinate cobalt(III) metal atoms, each in an octahedral environment. One cobalt(III) is coordinated to four azido ligands occupying the "equatorial" positions of the octahedron; the axial positions are occupied by trans ammine ligands. The second cobalt octahedron consists of four equatorial ammines and two trans azido ligands. A stereographic view of the molecule is provided in Figure 4. Each cobalt atom is situated on a center of symmetry, consistent with a special position in space group $P\bar{1}$.

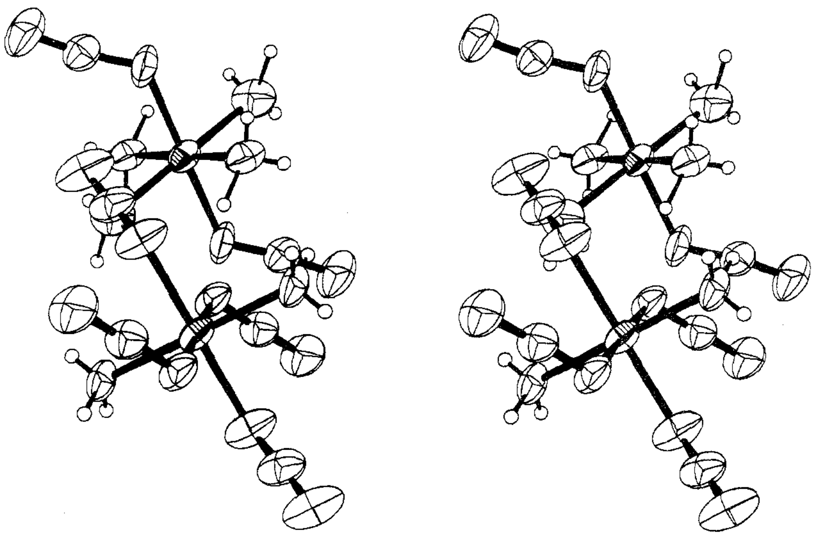

Figure 4. Stereoscopic ORTEP representation of [*trans*-$Co(NH_3)_4(N_3)_2$][*trans*-$Co(NH_3)_2(N_3)_4$].

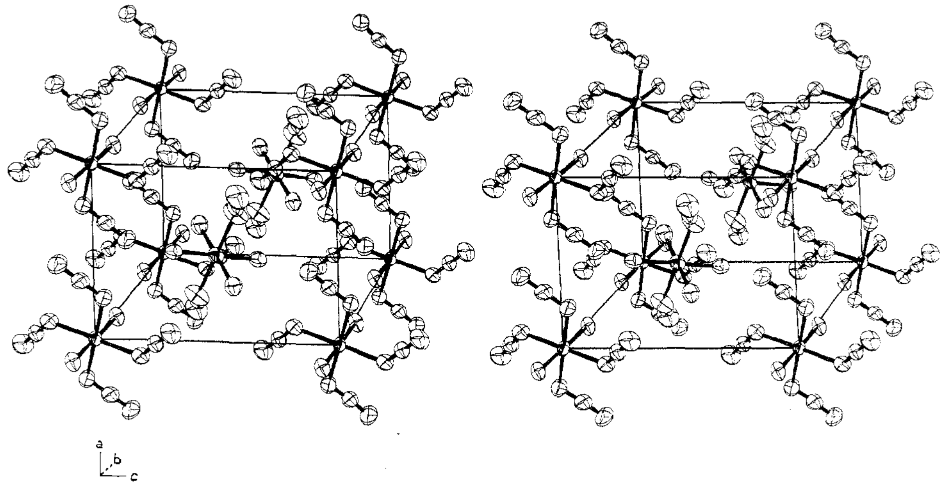

Figure 5. Stereoscopic representation of the unit cell.

The average $Co-NH_3$ bond distance is 1.980 (9) Å and is in agreement with values reported previously. The average $Co-N_3$ bond distance of 1.965 (9) Å is longer than reported by Palenik,[20] in $[Co(NH_3)_5(N_3)](N_3)_2$. The $Co(dien)(N_3)_3$ complex has a $Co-N_3$ bond distance of 1.947 Å.[8] The azido ligands in the tetraazido moiety have classical bond distances and angles. However, the azides of the diazide moiety are decidedly bent with bond angles of only 172.5 (12)°. This distortion may be in part due to hydrogen bonding of the linkage nitrogen to an ammine group in the adjacent tetraazide moiety and crystal packing forces (a similar hydrogen bonding network is also found in the structural analysis of $Co(dien)(N_3)_3$). Also of interest is the $Co'-N_8-N_9$ bond angle of 124.4 (9)°, a value identical with one found in the central azide of *mer*-$Co(dien)(N_3)_3$ and $[Co(NH_3)_5(N_3)](N_3)_2$.[8,18] In each of these analyses the linkage nitrogens were tightly hydrogen bonded to an adjacent molecule and were unique among the azido complexes in having relatively symmetric N–N distances.[8] Additional bond distances including suspected hydrogen bonds are tabulated in Table III; Tables I and II provide the atomic coordinates and anisotropic temperature factors for the complex. Figure 5 presents a stereographic representation of the packing diagram.

Infrared spectral results are shown in Figure 3. These results indicate subtle differences of the region 275–650 cm^{-1}. The azide deformational frequencies at 595 and 650 cm^{-1} appear symmetric and unsplit in *mer*-$Co(NH_3)_3(N_3)_3$, while substantially split for $[Co(NH_3)_4(N_3)_2][Co(NH_3)_2(N_3)_4]$.

The $Co-N(NH_3)$ stretching frequencies generally found as weak absorptions appear (for *trans*-$[Co(NH_3)_4X_2]X$ where X = Cl, the absorptions were positioned at 501 and 463 cm^{-1}; when X = Br, they were located at 486 and 465 cm^{-1}) at 420 and 495 cm^{-1} as singlets for $Co(NH_3)_3(N_3)_3$ and split for the polymerization isomer. Indeed the peak at 495 cm^{-1} for this isomer is similar to the equivalent vibration of the diazido complex (Figure 1). The intense N–M–N deformation is located at 350 cm^{-1} for all three complexes presented and cannot be used for any differentiation of the isomers.[21] The remaining strong absorption at 286 cm^{-1} is assigned to the $Co-N_3$ deformation. As was noted for the trinitrotriammines of cobalt(III), infrared spectroscopy does not provide strong indications of the geometry of these complexes. The PMR spectra of the two complexes (Figure 2) are more informative. The compound designated as the meridional isomer has two peaks, at 2.84 and 3.32 ppm, whose areas are in a ratio of 1:2, respectively. The first peak would correspond to the protons on the ammine trans to an azide while the second peak is assigned to the protons on the ammines trans to one another. (Since the second azido complex seemed to show only a single peak at 3.34 ppm, aside from the DMSO peak, it was originally assumed to be the facial isomer where each ammine is trans to an azide.)

Analysis of these complexes for azide by a polarographic technique used in this laboratory[9] resulted in the polarogram shown in Figure 3 which has two oxidation waves, due to two different types of azides whose ratio is approximately 1:2. The azide whose half-wave potential is 0.19 V is clearly one coordinated to a cobalt, while the larger potential of 0.34 V is well beyond those observed for free azide (normally found in the range 0.21–0.28 V). Together, these two waves correspond to an azide to cobalt molar ratio of 3:1.

The observed spectroscopic and polarographic evidence for this substance is in full agreement with the structural findings. In the polarographic studies, the azide whose half-wave potential is 0.19 V is clearly that of the cation; this potential agrees well with what was observed for *trans*-$[Co(NH_3)_4(N_3)](N_3)_2$. The larger wave is then due to the azides coordinated in the anionic complex. (Rather than deduce the infrared and electronic absorption spectra of the complex anion by subtracting the contribution of the known cation from the observed spectra of the polymerization isomer, attempts are being made to isolate the anion as a metallic salt.)

In theory, the PMR spectrum of the isomer might be expected to show two separate peaks. Thus far, it has not been possible to resolve this spectrum because of interference resulting from proton exchange with the DMSO (the only suitable solvent for this complex) and indirect coupling with the cobalt-59 nucleus.

It is obvious from the results of this investigation that there are circumstances when the traditional analytical methods cannot provide conclusive evidence for the structural identification of a coordination complex. In this case, single-crystal X-ray diffraction analysis provided the necessary information: that a hitherto unsuspected anionic complex ion resulted in the formation of the polymerization isomer *trans*-diazidotetraamminecobalt(III) *trans*-tetraazidodiamminecobaltate(III).

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Registry No. [*trans*-$Co(NH_3)_4(N_3)_2$][*trans*-$Co(NH_3)_2(N_3)_4$], 54689-17-7.

Supplementary Material Available. A table of observed and calculated structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036. Remit check or money order for \$4.00 for photocopy or \$2.50 for microfiche, referring to code number AIC40625K.

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Aryldiazo Complexes. Structure of an Iron–Aryldiazo Complex, $[Fe(CO)_2(N_2C_6H_5)(P(C_6H_5)_3)_2][BF_4]$

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The structure of $[Fe(CO)_2(N_2C_6H_5)(P(C_6H_5)_3)_2][BF_4]$ has been determined crystallographically. The compound crystallizes from acetone as solvent-free crystals in space group C_{2h}^5-$P2_1/c$ with a = 13.447 (4) Å, b = 14.260 (4) Å, c = 22.755 (16) Å, β = 113.29 (2)°, Z = 4, ρ_{exptl} = 1.37(1) g/cm^3, and ρ_{calcd} = 1.373 g/cm^3. Based on 3159 unique reflections with $F_o^2 > 3\sigma(F_o^2)$, the structure was solved and refined by full-matrix, least-squares methods to R = 0.064 and R_w = 0.088. The structure consists of discrete cations and anions; the BF_4 anions are partially disordered. The iron cation is five-coordinate with a coordination geometry close to trigonal bipyramidal. Apparently for steric reasons, the two carbonyl groups are nonequivalent. The phenyldiazo ligand in this complex is singly bent with Fe–N = 1.702 (6) Å, N–N = 1.201 (7) Å, N–C = 1.404 (8) Å, Fe–N–N = 179.2 (5)°, and N–N–C = 124.2 (6)°. The short Fe–N and N–N distances, as well as the general ligand geometry, suggest that multiple metal–nitrogen and nitrogen–nitrogen bonding is present and that the complex is best described as a PhN_2^+ complex of Fe(0). Structural and spectroscopic data suggest that the aryldiazo ligand is a good π acceptor but a poor σ donor.

Introduction

Aryldiazo ligands, as well as others which contain nitrogen–nitrogen multiple bonds, have been of great interest in recent years because of their close relationship to dinitrogen and nitrosyl ligands. Recently, structural and synthetic studies have shown the reaction chemistry of diazo ligands to be varied and interesting.[1–8] Especially noteworthy is the preparation of aroyl- and acyldiazo ligands from coordinated dinitrogen in rhenium, molybdenum, and tungsten complexes. Thus the close relationship between N_2 and RN_2 ligands, at least for