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Triamines of Cobalt(III). III. The Crystal Structures of *mer*-Triazidodiethylenetriaminecobalt(III), Co(dien) $(N_3)_3$

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Crystals of triazidodiethylenetriaminecobalt(III), [Co(dien) $(N_3)_3$], have space group $P\bar{1}$ with $a=8{\cdot}933$, $b=8{\cdot}973$, $c=8{\cdot}238$ Å, $\alpha=89{\cdot}90$, $\beta=113{\cdot}97$, $\gamma=73{\cdot}43°$ with two molecules per unit cell. The structure was determined from 1387 reflections with intensities significantly greater than background (Mo $K\alpha$ radiation), and refined by conventional least-squares methods to $R=5{\cdot}2$ %. An interesting feature of this crystal structure is disorder involving two conformers which differ in the orientation of the central azido ligand. One is coplanar with the amine nitrogens, a position favored in other amine complexes; in the second conformer, the azide is twisted out of the amine nitrogen plane by about 42°.

Introduction

In recent investigations of some azido complexes of cobalt(III), the most easily formed isomer of triazidodiethylenetriaminecobalt(III) was assigned the *meridional* configuration on the basis of infrared and proton magnetic resonance spectra (Druding, Wang, Cohen & Sancilio, 1973). An X-ray diffraction study of a crystal of this compound was undertaken to confirm the assigned structure.

Relatively few crystallographic studies of coordination complexes with an azide ligand have been reported. These include $[Co(NH_3)_5(N_3)](N_3)_2$ (Palenik, 1964), *trans*-$[Cu(NH_3)_2(N_3)_2]$ (Agrell, 1966), $Cu(N_3)_2$ (Söderquist, 1968) and $[Co(tetraen)(N_3](NO_3)_2.H_2O$ [tetraen = 4-(2-aminoethyl)-1,4,7,10-tetraazadecane] (Maxwell, 1971). Features common to these studies are an M–N–N bond angle of about 120° and N–N bond distances of approximately 1·20 Å (that nearest the metal) and 1·14 Å, as contrasted with the symmetrical bonds of 1·15 Å in the azide ion (Evans, Yoffe & Gray, 1959). The azide ligand in these complexes is located in a plane containing the metal atom and the other three coordinated nitrogen atoms. The structure of *cis*-$[Co(en)_2(N_3)_2](NO_3)$ was analyzed by two-dimensional X-ray diffraction data (Padmanabhan, Balasubramanian & Muralidharan, 1968). While not as refined as the other azido complex structural studies, this work gave the same values of the angle of attachment of the azido group to the metal and very similar N–N bond distances.

Triazidodiethylenetriaminecobalt(III) is relatively stable at room temperature and can be compressed to 15000 p.s.i. without evidence of decomposition, but it becomes a detonator when heated even moderately.

Experimental

WARNING: THE AZIDO COMPLEXES OF COBALT ARE EASILY DETONATED, ESPECIALLY SENSITIVE AT ELEVATED TEMPERATURES! USE EXTREME CAUTION WHEN HANDLING THE DRY SALTS - STORE IN SMALL QUANTITIES!

Data collection

mer-Triazidodiethylenetriaminecobalt(III) was prepared as previously described (Druding, Wang, Cohen & Sancilio, 1973). Although it decomposes readily in both hot water and on long standing in cold water, rapid crystallization from warm water is possible and yields well formed plates. These plates were obviously composed of twins, which could be mechanically separated. The crystal used was approximately 0·4 × 0·2 × 0·01 mm.

The lack of systematically absent reflections led to the assignment of space group $P1$ or $P\bar{1}$. Lattice constants were measured on a Hilger and Watts four-circle diffractometer using Ni-filtered Cu $K\alpha$ radiation ($\lambda=1{\cdot}5418$ Å). The intensity data were collected on the same instrument to $2\theta \leq 132{\cdot}6°$ using Zr-filtered Mo $K\alpha$ radiation ($\lambda=0{\cdot}7107$ Å) by the moving-crystal moving-dectector method. There were 1387 reflections measured with intensities significantly greater than background. Four standard reflections were monitored every 100 reflections to detect any crystal movement or decomposition; however, none was observed. The intensity data were corrected for Lorentz-polarization and absorption efecfts. The crystal data are given in Table 1.

Table 1. *Crystal data*

Formula $Co(C_4H_{13}N_3)(N_3)_3$, formula weight 288·152

Space group	$P\bar{1}$	Z	2
a	8·933 (16) Å	α	89·90 (8)°
b	8·973 (12)	β	113·97 (8)
c	8·238 (19)	γ	73·43 (8)
d_{obs}	1·703 g cm^{-3}	d_{calc}	1·699 g cm^{-3}
μ(Cu $K\alpha$)	100·60 cm^{-1}	μ(Mo $K\alpha$)	13·60 cm^{-1}

Solution of the structure

A three-dimensional Patterson map provided the position of the cobalt atom and successive Fourier syntheses revealed initial coordinates for all non-hydrogen atoms. Several least-squares cycles were run for both space groups. After two cycles, it became apparent that the structure was centrosymmetric and therefore belonged to space group $P\overline{1}$. After several additional cycles of both isotropic and anisotropic least-squares refinement of the nonhydrogen atoms, unusually high thermal parameters appeared for N(5) and N(6). (See Fig. 1 for numbering.) A Fourier difference synthesis, omitting these two atoms, revealed the existence of two atoms for each of the pair [designated N(5)*a*,N(6)*a* and N(5)*b*, N(6)*b*]. The discrepancy factors at this point were $R_1=11\cdot5\%$ and $R_2=16\cdot7\%$ where:

$$R_1=\sum ||F_o|-|F_c||/\sum F_o$$
$$R_2=[\sum ||F_o|-|F_c||^2/\sum w|F_o|^2]^{1/2}.$$

It became apparent that the N(5)*a* and N(6)*a* atoms were the predominant positions from their relative heights on the electron density map. The ratio of N(5)*a*:N(5)*b* was approximately 2:1, a ratio also observed for N(6)*a*:N(6)*b*.

After several further anisotropic least-squares cycles R_1 and R_2 converged to 6·1 and 8·4% respectively. A difference Fourier synthesis suggested the positions of the hydrogen atoms, which were placed assuming tetrahedral angles, and N–H, C–H bond lengths of 1·00 Å. R_1 converged to 5·2% and R_2 to 7·4%.

The least-squares calculations were performed using *ORFLS* and the atomic form factors were taken from Cromer & Waber (1965). The atomic coordinates from the final least-squares cycle are presented in Table 2. The anisotropic temperature factors appear in Table 3. Interatomic distances are presented in Table 4. Fig. 1 shows a stereoscopic drawing of *mer*-triazidodiethylenetriaminecobalt(III) along with the numbering system used. Fig. 2 illustrates the packing diagram of the molecules and the arrangement of the unit cell. A list of observed and calculated structure factors is available.*

Table 2. *Final atomic parameters for triazido(diethylenetriamine)cobalt*(III) *with standard deviations in parentheses*

	x	*y*	*z*	*B*
Co	0·18267 (12)	0·29795 (11)	0·35325 (12)	*
N(1)	0·1135 (8)	0·5138 (7)	0·2421 (8)	*
N(2)	0·1799 (8)	0·6027 (8)	0·3311 (9)	*
N(3)	0·2404 (14)	0·6917 (11)	0·4184 (12)	*
N(4)	0·2501 (8)	0·3590 (8)	0·5899 (9)	*
N(5)*a*	0·3841 (13)	0·2904 (15)	0·7091 (14)	*
N(5)*b*	0·3844 (24)	0·3821 (26)	0·6748 (25)	*
N(6)*a*	0·5108 (18)	0·2277 (21)	0·8284 (19)	*
N(6)*b*	0·5163 (30)	0·4096 (46)	0·7659 (36)	*
N(7)	0·2562 (9)	0·0757 (7)	0·4505 (9)	*
N(8)	0·2113 (8)	0·0415 (7)	0·5600 (8)	*
N(9)	0·1714 (10)	0·0018 (10)	0·6655 (10)	*
N(10)	0·4076 (7)	0·2457 (8)	0·3429 (8)	*
N(11)	0·0980 (7)	0·2463 (7)	0·1115 (8)	*
N(12)	−0·0520 (7)	0·3291 (7)	0·3304 (8)	*
C(1)	0·3867 (11)	0·2127 (10)	0·1612 (11)	*
C(2)	0·2424 (12)	0·1418 (10)	0·0854 (11)	*
C(3)	−0·0550 (10)	0·1922 (9)	0·0788 (10)	*
C(4)	−0·1628 (9)	0·3119 (9)	0·1466 (10)	*
H(1)1	0·497	0·140	0·165	5·0
H(1)2	0·356	0·314	0·083	5·0
H(2)1	0·210	0·132	−0·046	5·0
H(2)2	0·279	0·033	0·151	5·0
H(3)1	−0·017	0·085	0·146	5·0
H(3)2	−0·120	0·188	−0·053	5·0
H(4)1	−0·213	0·416	0·068	5·0
H(4)2	−0·261	0·278	0·146	5·0
H(N10)2	0·455	0·336	0·374	5·0
H(N10)1	0·491	0·151	0·432	5·0
H(N11)	0·055	0·346	0·027	5·0
H(N12)2	−0·049	0·249	0·417	5·0
H(N12)1	−0·099	0·436	0·358	5·0

* Anisotropic thermal parameters are given in Table 3.

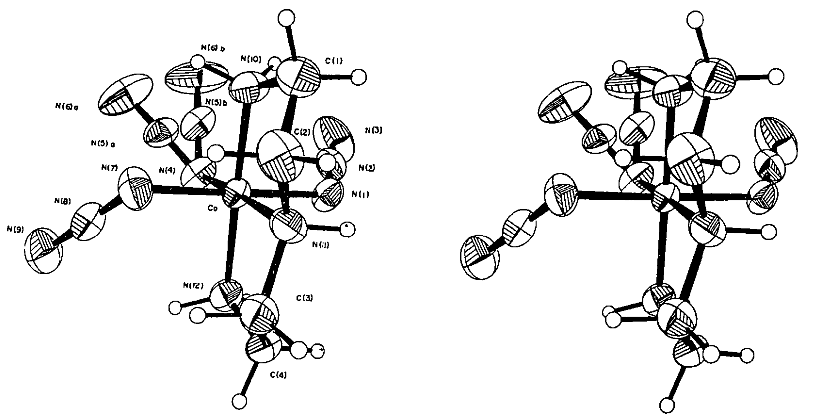

Fig. 1. Stereo view of triazidodiethylenetriaminecobalt(III). The thermal ellipsoids of the non-hydrogen atoms are scaled to 50% probability. The hydrogens are shown as spheres of arbitrary size.

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* This table has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30516 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Discussion

The average value of 1·96 Å for the distance between the cobalt(III) and the *trans*-amine nitrogen atoms agrees well with those values reported by other observers. The distance of 1·93 Å for the secondary amine nitrogen (–NH–) to cobalt distance is identical with that reported by Gainsford, House & Robinson (1971) in the *meridional* isomer of [Co(dien)(en)(Cl)]($ZnCl_4$).

The average cobalt–azide distance was found here to be 1·947 Å; Palenik (1964) reported a distance of 1·943 Å in [$Co(NH_3)_5(N_3)$](N_3)$_2$, and Padmanabhan *et al.* (1968) reported 1·97 Å for [$Co(en)_2(N_3)_2$](NO_3); however the latter determination is less accurate.

The azide group is slightly bent with an average N–N–N angle of 177°, similar to observations in the other azido complexes cited. The *trans* azides in the complex are asymmetric with respect to their nitrogen–nitrogen bond distances with average values of 1·20 and 1·16 Å (with the latter distance being between the nitrogens not bonded to the metal).

The cobalt to nitrogen bond angles are in agreement with expectations. The chelate rings of the diethylenetriamine show a distortion of the N(10)–Co–N(12) angle to 170.4°, and of the N(11)–Co–N(12) angle to 85·6°, as has been observed for *mer*-[Co(dien) (en)Cl]-($ZnCl_4$). The dien group is symmetric with respect to the Co–N(11) axis, which was also found in a solution analysis of the ^{13}C n.m.r. spectrum. This compound

Table 4. *Bond lengths* (Å) *with standard deviations in parentheses*

(*a*) Non-hydrogen atoms

Co––N(1)	1·954 (6)	N(5)*a*–N(6)*a*	1·137 (19)
Co—N(4)	1·922 (7)	N(5)*b*–N(6)*b*	1·206 (34)
Co––N(7)	1·966 (6)	N(7)—N(8)	1·196 (9)
Co––N(10)	1·964 (6)	N(8)—N(9)	1·153 (10)
Co––N(11)	1·930 (6)	N(10)–C(1)	1·472 (10)
Co––N(12)	1·960 (6)	C(1)––C(2)	1·505 (12)
N(1)–N(2)	1·201 (9)	C(2)—N(11)	1·457 (10)
N(2)–N(3)	1·173 (11)	N(11)–C(3)	1·500 (10)
N(4)–N(5)*a*	1·181 (14)	C(3)––C(4)	1·400 (10)
N(4)–N(5)*b*	1·195 (25)	N(12)–C(4)	1·471 (10)

(*b*) Intermolecular hydrogen bonding distances

N(1)····N(11)	3·14
N(3)····N(10)	3·17
N(3)····N(12)	3·18
N(4)····N(12)	3·08
N(5)*a*···N(10)	3·12

Table 3. *Final anisotropic thermal parameters* (× 10^4) *for triazido*(*diethylenetriamine*)*cobalt*(III) *with standard deviations in parentheses*

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

	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Co	103 (2)	79 (1)	114 (2)	−18 (1)	42 (1)	−7 (1)
N(1)	138 (11)	82 (8)	154 (12)	−37 (8)	19 (9)	−4 (8)
N(2)	176 (13)	129 (10)	194 (14)	−72 (10)	81 (11)	−2 (10)
N(3)	427 (27)	247 (18)	303 (22)	−241 (20)	181 (21)	−112 (17)
N(4)	139 (12)	125 (10)	168 (13)	−16 (9)	30 (11)	−24 (9)
N(5)*a*	120 (20)	148 (18)	156 (22)	−5 (16)	61 (18)	−18 (16)
N(5)*b*	155 (38)	145 (30)	131 (35)	−2 (27)	50 (30)	−33 (27)
N(6)*a*	185 (26)	323 (36)	248 (31)	19 (26)	7 (25)	−68 (26)
N(6)*b*	158 (42)	555 (93)	286 (57)	−146 (51)	56 (41)	−232 (60)
N(7)	197 (13)	94 (9)	212 (14)	−15 (9)	136 (12)	−5 (9)
N(8)	137 (11)	105 (9)	158 (13)	−7 (8)	47 (10)	2 (9)
N(9)	245 (16)	194 (14)	196 (15)	−63 (12)	113 (14)	28 (11)
N(10)	105 (10)	144 (10)	173 (13)	−31 (8)	53 (9)	−19 (9)
N(11)	121 (10)	108 (9)	184 (12)	−39 (8)	77 (10)	−2 (8)
N(12)	119 (10)	105 (8)	149 (11)	−22 (7)	52 (9)	−15 (8)
C(1)	157 (14)	168 (14)	193 (17)	−21 (11)	107 (14)	−8 (12)
C(2)	220 (17)	147 (13)	166 (15)	−63 (12)	112 (14)	−48 (11)
C(3)	150 (14)	118 (11)	158 (14)	−57 (10)	49 (12)	−10 (10)
C(4)	102 (11)	123 (11)	181 (15)	−35 (9)	19 (11)	17 (10)

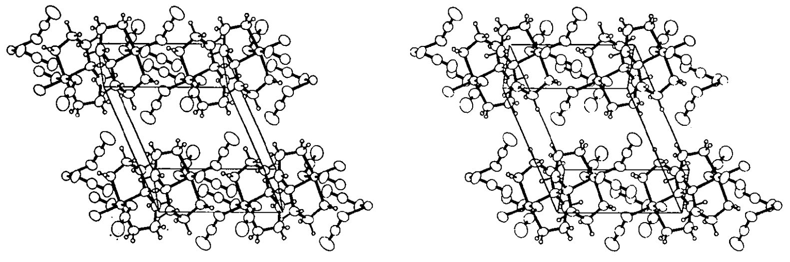

Fig. 2. Packing diagram (stereo view, with the *c* axis towards the rear in a right-handed coordinate system) of triazidodiethylenetriaminecobalt(III). Note that the *c* axis has been halved to simplify viewing.

seemed to show the existence of a mirror plane coincident with the Co–N(1)–N(4) plane indicating free rotation of the azide ligands (Druding, Lukaszewski & Sancilio, 1974).

The bond angles of the coordinated azides *trans* to one another average 118·3°, which is typical of those azido coordination complexes studied so far, but the central azide group exhibits angles of both 121·5 and 124·4°. The latter angle approaches that found by Palenik (1964) for the azidopentaamminecobalt(III) ion while the former is more typical of the angle found in covalently bonded azides (Dori & Ziolo, 1973).

The distribution of the central azide over the two positions is in the approximate proportion 2:1. The azide group designated '*a*' is twisted approximately 43° from the plane of the dien nitrogens, and away from the nearest terminal azide group. A first assumption was that this configuration was favored because of a minimal amount of steric hindrance to the neighboring ligands, but upon calculation of non-bonded interactions, little differences are seen for either position. In the second configuration, designated '*b*', the azide ligand is coplanar with the three nitrogens of the dien group. Maxwell (1971) suggested the possibility of orbital overlap between an azide π^* orbital and a cobalt d_{xy} orbital, which may account for this configuration. Such an arrangement is found in $[Co(tetraen)(N_3)](NO_3)_2$ and $[Cu(NH_3)_2(N_3)_2]$.

In position '*a*', the cobalt–azide angle is 121·5°. The azide is unsymmetrical with N–N distances of 1·18 and 1·14 Å. These shorter distances resemble those of the azide ion. Although the σ value for the coplanar conformation is rather large, the azide seems symmetrical with N–N bond distances of 1·20 and 1·21 Å and a cobalt–azide angle of 124·4°.

An interesting parallel to these azido conformers has been found in the conformational isomers of *mer*-$[Co(en)(NH_3)(NO_2)_3]$ (Jensen, Soling & Thorup, 1970). Two polymorphic forms of the compound were obtained. In the brown form, the three atoms of the nitro group in the 2-position are approximately coplanar with the (en) and (NH_3) nitrogens bonded to cobalt, while in the yellow form, this nitro group is oriented 31° out of the plane (MacDermott & Barjoed, 1970). Gross differences in these two conformations allow crystallization of each of the two conformers to occur. This type of rotational isomerization may be common in cobalt(III)–amine complexes where positions of maximum orbital overlap are possible.

The packing of the complex involves hydrogen bonding through the linkage nitrogen of the azide, as can be seen from the distances in Table 4(*b*).

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