difficult to account for these observed variations in terms of systematic errors in the two structure determinations since the cell dimensions, space groups and crystal structures of the two materials are completely different.

There appear to be some similarities between corresponding bond angles in the two molecules but the agreement is much less obvious than the agreement between bond lengths.

The carbon atoms linking the two aromatic rings, C(1) and C(1'), are separated by a distance ($1\cdot515 \pm 0\cdot024$ Å) in the dichloro-molecule which is not significantly different from that observed in the dimethyl molecule ($1\cdot504 \pm 0\cdot013$ Å) and in biphenyl itself ($1\cdot497 \pm 0\cdot003$ Å) and which probably represents a $C(sp^2)$–$C(sp^2)$ single bond.

The chlorine and nitrogen atoms are attached to the aromatic rings by bonds of normal lengths but all four atoms are displaced out of the planes of the rings and for ring II (Table 3) the displacements appear to be significant.

Fig. 4(a) and (b) show the structure viewed along the directions [010] and [100] respectively and indicate all distances of $4\cdot0$ Å or less between atoms in neighbouring molecules. The shortest distances are $3\cdot23$ and $3\cdot30$ Å between two pairs of nitrogen atoms, $3\cdot35$ and $3\cdot35$ Å between two pairs of chlorine atoms, and $3\cdot51$ Å between a pair of carbon atoms.

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The Structure of cis-Cobalt Diazidobisethylenediamine Nitrate, Co(C2N2H8)2(N3)2NO3

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The crystal structure of cis-cobalt diazidobisethylenediamine nitrate has been determined from two-dimensional X-ray diffraction data. The cell has dimensions $a = 12\cdot106$, $b = 23\cdot620$, $c = 8\cdot801$ Å, space group Pnma and $Z = 8$. The cobalt ion has a distorted octahedral coordination with four N atoms of the ethylenediamine group and two N atoms of the azide group. The ethylenediamine molecule is in gauche configuration. The azido groups are linear with N–N distances $1\cdot11$–$1\cdot23$ Å. The valence angle Co–N–N is $\sim 120°$. The two nitrate ions are stacked one above the other to form a close packing with the complex ions.

Very few structures of compounds coordinating an azide group have been reported in the literature. The present note describes the structure of a cobalt compound coordinating ethylenediamine and azide groups.

Orthorhombic crystals of the cobalt complex were obtained from solution by the method described by Staples & Tobe (1960). Crystal data were determined from various rotation and Weissenberg films using Fe $K\alpha$ radiation, and were as follows:

$a = 12\cdot106 \pm 0\cdot010$, $b = 23\cdot620 \pm 0\cdot010$, $c = 8\cdot801 \pm 0\cdot01$ Å
D_o (flotation method) $= 1\cdot60$, $Z = 8$, $D_c = 1\cdot58$ g.cm^{-3}.

The space group is Pnma or Pna2$_1$. Pnma was confirmed by the structure analysis.

The intensities of the $hk0$, $0kl$ and $h0l$ reflexions were measured visually from Weissenberg films from crystals rotating about the three respective axes. The position of the cobalt atom was determined from Patterson projection maps, and from a series of four electron-density projections the coordinates of all the other atoms were determined. The structure was refined by least squares on the CDC 3600 computer. The final R value for 293 reflexions was $0\cdot10$. The atomic co-

ordinates, the temperature factors and their e.s.d. are given in Table 1. The bond lengths and angles are listed in Table 2. The estimated standard deviation in bond lengths is 0·02 Å and in angles 1·8°.

The coordination of the cobalt ion is the usual distorted octahedral configuration with four nitrogen atoms from the two ethylenediamine molecules at 2·00 Å and two nitrogens from the two azide groups at 1·97 Å.

The bond directions in the coordination polyhedron deviate slightly from 90° ranging from 84°–92°. The ethylenediamine molecule is in the *gauche* configuration and the bond distances and angles in the molecule appear to be normal, and compare well with those reported earlier in the literature.

The azide groups, as mentioned above, complete the octahedral configuration around cobalt with their ni-
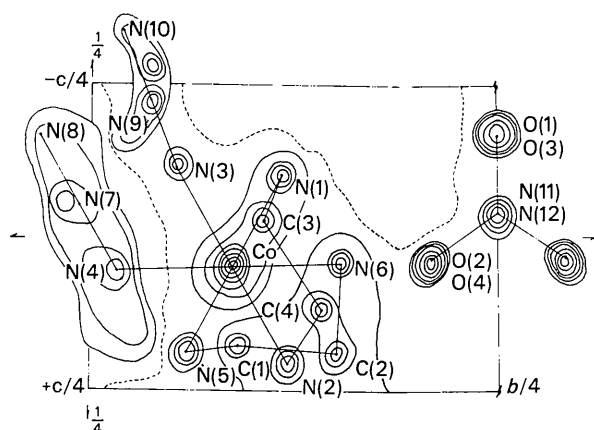
Table 1. *Atomic parameters*

	x	y	z	B
Co	0·248	0·087	0·045	0·87
C(1)	0·033	0·090	0·178	5·42
C(2)	0·078	0·150	0·188	2·93
N(5)	0·145	0·059	0·210	2·32
N(6)	0·141	0·152	0·039	1·63
C(3)	0·463	0·102	−0·028	4·28
C(4)	0·447	0·141	0·117	1·24
N(1)	0·351	0·118	−0·102	1·10
N(2)	0·350	0·120	0·208	1·50
N(3)	0·153	0·053	−0·114	1·50
N(9)	0·186	0·041	−0·226	1·09
N(10)	0·202	0·018	−0·338	1·01
N(4)	0·330	0·016	0·055	1·96
N(7)	0·357	−0·009	−0·048	2·47
N(8)	0·393	−0·030	−0·166	1·50
N(11)	0·923	0·250	−0·053	1·50
O(1)	0·911	0·250	−0·018	1·54
O(2)	0·920	0·211	0·036	1·01
N(12)	0·621	0·250	−0·040	1·50
O(3)	0·636	0·250	−0·185	1·52
O(4)	0·633	0·205	0·046	2·04

Average standard deviations

	x	y	z	B
Co	0·0006	0·0006	0·001	0·20
C	0·004	0·002	0·005	0·31
N	0·003	0·002	0·004	0·18
O	0·002	0·001	0·004	0·26

Fig. 1. Electron-density projection along **a** (contour level arbitrary).
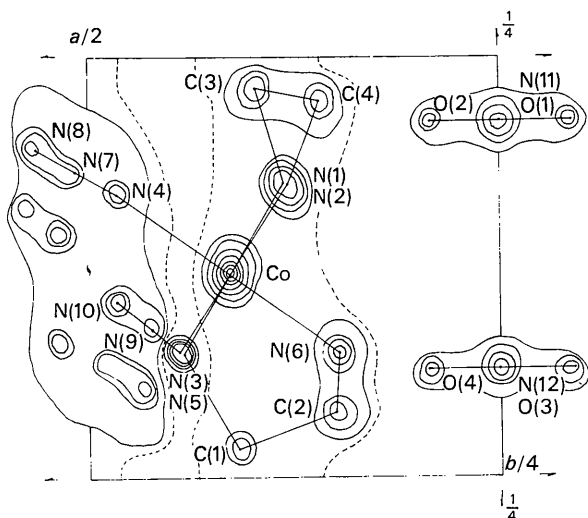
Fig. 2. Electron density projection along **c**.

Table 2. *Bond distances and angles*

Co——N(1)	1·95 Å	N(1) Co N(2)	87°
Co——N(2)	2·03	N(1) Co N(3)	92
Co——N(3)	1·99	N(1) Co N(4)	91
Co——N(4)	1·95	N(1) Co N(6)	95
Co——N(5)	2·03	N(2) Co N(4)	92
Co——N(6)	1·99	N(2) Co N(6)	91
C(1)—C(2)	1·52	N(2) Co N(5)	91
C(3)—C(4)	1·58	N(3) Co N(4)	89
N(1)—C(3)	1·53	N(3) Co N(5)	89
N(2)—C(4)	1·51	N(3) Co N(6)	85
N(5)—C(1)	1·54	N(4) Co N(5)	88
N(6)—C(2)	1·51	N(4) Co N(6)	84
N(3)—N(9)	1·11	Co N(5) C(1)	107
N(9)—N(10)	1·14	Co N(6) C(2)	107
N(4)—N(7)	1·14	N(6) C(2) C(1)	101
N(7)—N(8)	1·23	N(5) C(2) C(1)	101
N(11)–O(1)	1·20	Co N(1) C(3)	102
N(11)–O(2)	1·22	Co N(2) C(4)	106
N(12)–O(3)	1·26	N(1) C(3) C(4)	101
N(12)–O(4)	1·28	N(2) C(4) C(3)	108
		N(4) N(7) N(8)	179
		N(3) N(9) N(10)	179
		O(1) N(11) O(2)	125
		O(3) N(12) O(4)	127
		Co N(4) N(7)	119
		Co N(3) N(9)	120

trogen atoms. Except for the structure of azidopentammine cobalt azide (Palenik, 1964) no work has so far been reported on the structure of coordination compounds bonding the azido group. Within the limits of experimental error the azido groups appear to be linear. The N–N distances in each group are not equal. Palenik (1964) has reported that the azide group in

the coordination sphere is asymmetric with N–N distances 1·15 and 1·21 Å. The valence angle Co–N–N is 120°. From infrared studies Staples & Tobe (1960) have suggested that the valence angle should be in the region 108°–120°. In azidopentamminecobalt azide this angle is 124°. The arrangement of the nitrate ions is interesting; two ions are stacked one above the other at $y=\frac{1}{4}$. Swink & Atoji (1960) have reported such an arrangement in $Ni(en)_3(NO_3)_2$, where the two nitrate ions are stacked one above the other to give close packing with ethylenediamine ions. The NO_3 group is planar. The average N–O distance is 1·24 Å in agreement with the standard empirical value.

The contact distances between non-bonded atoms appear to be reasonable. These distances range upwards from 3·20 Å except for the distance 2·75 Å, between C(2) of the ethylenediamine group and O(2) of the nitrate ion. As the structure is obtained from projection data, no special comment is made regarding this short C–H⋯O distance.

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The Crystal Structure of Ferricinium Triiodide, (C5H5)2FeI3*

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Ferricinium triiodide crystallizes in the trigonal system with probable space group $R\bar{3}m$. The rhombohedral unit cell has dimensions $a_R = 7·517 \pm 5$ Å, $\alpha_R = 69°4' \pm 10'$ and contains one unit of $(C_5H_5)_2FeI_3$. The trial structure was determined from symmetry considerations and verified by comparison of calculated and observed structure factors for 159 independent reflexions (intensities measured by photometry of precession photographs). Coordinates and Debye–Waller factors of all atoms other than hydrogen were refined by least squares, the final R index being 11·3%. The structure is similar to that of CsCl, but with the unit cell elongated along $[111]_R$. The ferricinium cation is centred at the origin, with the cyclopentadiene rings perpendicular to the threefold axis in a disordered arrangement. The triodide anion is centered at $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$ and lies along the threefold axis. The triodide anion thus appears to be symmetrical and linear, with $d(I-I) = 2·93 \pm 0·02$ Å. The disorder of the crystal makes it impossible to draw detailed conclusions about the structures of the cation and perhaps the anion. Diffraction photographs at 130°K showed no evidence of a phase change having occurred between 300°K and 130°K.

Introduction

Ferrocene forms a number of compounds with iodine; compositions FcI_n (Fc = ferrocene) have been reported with $3 \leq n \leq 20$ (Nesmeyanov, Paravahova & Nesmeyanova, 1955; Cais & Adam, 1967). We have carried out a three-dimensional crystal structure analysis of the first member of the series $(n=3)$ and the results show that this compound is ferricinium triiodide. The detailed atomic arrangements in ferrocenes and in ferricinium and trihalide ions have been the subject of many investigations, both experimental and theoretical, but disorder in the ferricinium triiodide crystals limits the information that can be obtained from this study about the detailed structures of the ions.

Experimental

Our crystals were prepared (by Mr M. Adam) by solution of FcI_6 in acetone and subsequent slow evaporation of the solvent; black rhombohedra,* stable in air, were deposited. The angles between the faces were $82 \pm \frac{1}{2}°$ and the faces were subsequently indexed as $\{110\}_R$.

Oscillation, Weissenberg and precession photographs were taken of crystals mounted about the long diagonal of the rhombohedron (the hexagonal c axis) and oscillation and Weissenberg photographs about an axis normal to this diagonal (*i.e.* about the hexagonal a axis). Trigonal symmetry was evident from the first set of photographs while the second set showed

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* Based on the M. Sc. thesis of T. Bernstein, accepted by the Senate of the Technion – Israel Institute of Technology, 1967.

* We shall mostly use hexagonal axes in the description of our results; when rhombohedral axes are used, they will be denoted by a subscript R.