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The Crystal Structure of Catena-di-μ-hydrazine-Zinc Diacetate

By A. Ferrari, A. Braibanti, G. Bigliardi and A. M. Lanfredi

Centro di Strutturistica Roentgenografica del C. N. R., Sezione di Parma, 1° Reparto. – Istituto di Chimica generale e Istituto di Mineralogia dell'Università di Parma, Italy

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The crystal structure of catena-di-μ-hydrazine-zinc diacetate has been determined. The refinement has been carried out by three-dimensional differential syntheses. The structure is composed of chains of slightly distorted octahedral complexes $[Zn(N_2H_4)_{4/2}(CH_3COO)_2]$. The distances between zinc and nitrogen are Zn–N(1) = 2·179 Å and Zn–N(2) = 2·206 Å and the distance between zinc and oxygen is Zn–O(1) = 2·147 Å. The octahedra are held together in the chain by two bridges of hydrazine. The hydrazine molecule is staggered and the distance between nitrogen atoms is N(1)–N(2) = 1·458 Å. The acetate group is perfectly planar. The distances C(1)–O(1) = 1·264 Å and C(1)–O(2) = 1·250 Å are comparable to those in similar compounds in which the environments of O(1) and O(2) are equivalent.

Introduction

The crystal structures of compounds with general formula $[M^{II}(N_2H_4)_2]X_2$, where M^{II} = Cd,Zn,Ni,Co,Fe,Mn and X = Cl,NCS,Br,I,CH_3COO, *etc.* present the common feature of being formed by chains of complexes $[M^{II}(N_2H_4)_{4/2}X_2]$ extending throughout the crystal in one direction (Ferrari, Braibanti & Bigliardi, 1962, 1963; Ferrari, Braibanti, Bigliardi & Dallavalle, 1963; Ferrari, Braibanti, Bigliardi & Lanfredi, 1965). Therefore, these compounds can be considered as catena-di-μ-hydrazine-divalent-metal salts, $[M^{II}(N_2H_4)_2]_nX_{2n}$ (*Nomenclature of Inorganic Chemistry*, 1959). The crystals are very often twinned.

A thorough examination of this class of structure has been undertaken in order to clarify some important aspects of the chemical bonds implied in them and, moreover, to explain, if possible, the twinning laws or the absence of twinning on a structural basis (Braibanti, Bigliardi, Lanfredi & Camellini, 1964).

The study of the crystal structure of catena-di-μ-hydrazine-zinc diacetate, $[Zn(N_2H_4)_2]_n(CH_3COO)_{2n}$, is presented here.

Experimental

The crystals of $[Zn(N_2H_4)_2]_n(CH_3COO)_{2n}$ were obtained by mixing aqueous ammonia, hydrazine hydrate and an aqueous solution of zinc acetate (Ferrari, Braibanti, Bigliardi & Lanfredi, 1963). The crystals are often, but not always, twinned and are isostructural with the corresponding cadmium and manganese compounds.

The unit-cell constants have been found to be: $a = 6{\cdot}58 \pm 0{\cdot}02$, $b = 8{\cdot}52 \pm 0{\cdot}01$, $c = 4{\cdot}14 \pm 0{\cdot}01$ Å; $\alpha = 90°$, $\beta = 90° 25' \pm 5'$, $\gamma = 96° 52' \pm 12'$.

One stoichiometric unit $[Zn(N_2H_4)_2](CH_3COO)_2$ is contained in the unit cell. The calculated and observed density are: $\varrho_c = 1{\cdot}783$ g.cm^{-3}, $\varrho_o = 1{\cdot}798$ g.cm^{-3}. The space group is $P\bar{1}$.

The intensities of the reflexions $hk0$, $hk1$, $hk2$, $hk3$ were taken by rotating a very thin needle around [001]. A Weissenberg camera (Cu $K\alpha$ radiation) was used, the multiple-film technique being applied. The blackening of the integrated spots was determined by a microphotometer. (Observed reflexions: 788). The corrections for polarization, Lorentz and transmission factors were calculated by an Olivetti Elea 6001/S computer. For the calculation of the transmission factors a cylindrical shape of the crystal has been assumed ($\mu R = 0{\cdot}33$). The atomic form factors were calculated by the computer using the Forsyth & Wells (1959) formula, with the constants given by Moore (1963).

Determination and refinement of the structure

The structure was first determined by a Patterson projection $P(UV)$; successive Fourier syntheses $\varrho_o(xy)$, where all the peaks are well resolved, led to a disagreement index $R_{hk0} = 0{\cdot}17$.

The z coordinates were found by generalized Patterson functions ${}_CP_1(UV)$ and ${}_SP_1(UV)$. All the coordinates were refined by differential syntheses (Booth, 1964), following the method described by Nardelli, Fava & Giraldi (1963). Isotropic temperature factors were used at this stage. A three-dimensional $(\varrho_o - \varrho_{Hv})(xyz)$ (where the subscript $_{Hv}$ means heavy atoms), gave maxima in satisfactory agreement with the positions of hydrogen atoms, calculated assuming a staggered form for hydrazine (Penney & Sutherland, 1934; Ferrari, Braibanti & Bigliardi, 1963; Ferrari, Braibanti, Bigliardi & Dallavalle, 1963; Ferrari, Braibanti, Bigliardi & Lanfredi, 1965). Also the hydrogen atoms of the methyl group can be located on density peaks, resembling roughly a nearly tetrahedral configuration of bonds around carbon. The total disagreement index was at this stage $R_{hkl} = 0{\cdot}114$. At this point anisotropic temperature factors were introduced and refined (Nardelli, Fava & Giraldi, 1963). Differential syntheses and anisotropic temperature factor refinement were applied

Table 1. *Atomic positional parameters*

Atom	x	$\sigma(x)$	y	$\sigma(y)$	z	$\sigma(z)$
Zn	0·0000	0·0000	0·0000	0·0000	0·0000	0·0000
C(1)	0·7486	0·0008	0·2820	0·0008	0·8862	0·0024
C(2)	0·7434	0·0012	0·4509	0·0011	0·7637	0·0034
N(1)	0·2428	0·0007	0·0440	0·0008	0·6445	0·0021
N(2)	0·1955	0·0007	0·1360	0·0007	0·3626	0·0021
O(1)	0·9138	0·0007	0·2232	0·0006	0·8438	0·0018
O(2)	0·5915	0·0007	0·2148	0·0007	0·0183	0·0024
Probable position of hydrogen atoms *						
H(1)	0·6916		0·1039		0·4742	
H(2)	0·3365		0·0922		0·8270	
H(3)	0·3056		0·1509		0·1409	
H(4)	0·0913		0·2057		0·4112	
H(5)	0·5808		0·4220		0·6414	
H(6)	0·0922		0·4637		0·3278	
H(7)	0·1901		0·4898		0·0000	

* Error undetermined

alternately. In a few cycles the agreement improved to $R_{hkl}=0\cdot093$ (observed reflexions); $R_{hkl}=0\cdot096$ without hydrogen atom contributions. In the three-dimensional $(\varrho_o-\varrho_{Hv})$ (xyz), maxima can be reasonably, but not certainly, assigned to the hydrogen atoms (Fig. 1).

The numerical results of the structural determination are given in Tables 1, 2, 3, 4. The standard deviations of distances and angles (Table 4) were calculated by the methods of Ahmed & Cruickshank (1953) and Darlow (1960) respectively. The coordinates of the hydrogen atoms are quoted with as many figures as those introduced in the last structure factor calculation. Their location can be considered as a reasonable hypothesis, consistent with the experimental data, and no assessment of the accuracy is possible; therefore coordinates of the hydrogen atoms, and distances and angles involving hydrogen atoms as well, are quoted as obtained from the calculations, without any particular rounding off of the figures.

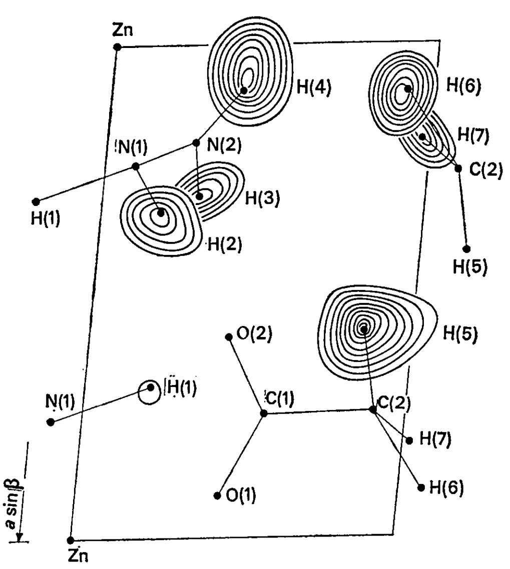


Fig. 1. $(\varrho_o-\varrho_{Hv})(xyz)$ viewed down [001]. Composite map; only those maxima are drawn which can be reasonably assigned to hydrogen atoms. Intervals every 0·05 e.Å^{-3}, starting at 0·3 e.Å^{-3}.

Discussion of the structure

Coordination complex and chains of complexes

A diagramatic projection of one layer of the structure, parallel to (001), is shown in Fig. 2. The complex $[Zn(N_2H_4)_{4/2}(CH_3COO)_2]$ is of octahedral type. The nitrogen atoms of the complex belong to four different hydrazine molecules. The distances between zinc and nitrogen are Zn–N(1) = 2·179 ± 0·007 Å and Zn–N(2) = 2·206 ± 0·007 Å, and the distance between zinc and oxygen is Zn–O(1) = 2·147 ± 0·005 Å. These can be compared with corresponding distances in other octahedral complexes of zinc. Distances quoted in the literature are for Zn–N: 2·170 Å, 2·186 Å (Ferrari, Braibanti, Bigliardi & Lanfredi, 1965), 2·099 Å (Palenik, 1964), 2·15 Å (Ferrari, Braibanti & Bigliardi, 1963), 2·00 Å (Doyne & Pepinsky, 1957); for Zn–O: 2·123 Å, 2·075 Å (Montgomery & Lingafelter, 1964), 2·066 Å, 2·263 Å (Palenik, 1964), 2·10 Å (Ghose, 1964), 2·039 Å

Table 2. *Thermal atomic parameters* (Å^2)*

	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Zn	1·534	1·845	1·152	0·161	0·220	0·112
C(1)	1·772	1·800	0·897	$\overline{0\cdot045}$	0·165	0·110
C(2)	3·601	2·386	2·786	0·748	0·614	1·075
N(1)	1·434	2·382	0·752	0·328	0·046	0·269
N(2)	0·960	1·967	1·214	0·231	0·077	$\overline{0\cdot143}$
O(1)	2·325	2·012	1·591	0·530	0·611	0·761
O(2)	4·381	3·379	1·467	1·054	0·786	$\overline{0\cdot084}$

The hydrogen atoms have been given the last isotropic temperature factor of the atom to which they are bound:

	H(1)	H(2)	H(3)	H(4)	H(5)	H(6)	H(7)
B	1·65	1·65	1·50	1·50	2·65	2·65	2·65

* Error undetermined. Average and maximum thermal parameter shift in the last cycle: Zn|0·005| (av.), |0·008| (max.); C(1) |0·011|, |0·036|; C(2) |0·047|, |0·099|; N(1) |0·011|, |0·017|; N(2) |0·010|, |0·025|; O(1) |0·028|, |0·059|; O(2) |0·037|, |0·094|.

Table 3. *Observed and calculated structure factors*

h	k	l	$10F_o$	$10F_c$
1	0	0	218	327
2	0	0	44	10-
3	0	0	199	164
4	0	0	229	246
5	0	0	207	195
6	0	0	—	17-
7	0	0	70	73
8	0	0	95	101
0	1	0	235	430
1	1	0	319	430
1	1-	0	152	158
2	1	0	142	128
2	1-	0	233	254
3	1	0	291	313
3	1-	0	—	41
4	1	0	237	216
4	1-	0	128	126
5	1	0	262	244
5	1-	0	134	112
6	1	0	102	86
6	1-	0	134	127
7	1	0	—	1
7	1-	0	145	148
8	1	0	76	86
8	1-	0	52	59
0	2	0	137	115
1	2	0	—	43
1	2-	0	388	441
2	2	0	—	31
2	2-	0	124	124
3	2	0	327	351
3	2-	0	—	15
4	2	0	305	305
4	2-	0	248	243
5	2	0	108	108
5	2-	0	204	189
6	2	0	120	129
6	2-	0	190	191
7	2	0	81	87
7	2-	0	103	99
8	2	0	86	99
8	2-	0	81	87
0	3	0	54	62
1	3	0	—	10
1	3-	0	391	424
2	3	0	134	135
2	3-	0	232	232
3	3	0	160	166
3	3-	0	283	284
4	3	0	255	239
4	3-	0	232	213
5	3	0	—	50
5	3-	0	168	170
6	3	0	58	72
6	3-	0	156	145
7	3	0	126	129
7	3-	0	46	52
8	3-	0	89	95
0	4	0	386	342
1	4	0	94	104
1	4-	0	368	320
2	4	0	246	229
2	4-	0	193	186
3	4	0	162	152
3	4-	0	272	255
4	4	0	147	137
4	4-	0	154	161
5	4	0	—	47
5	4-	0	145	145
6	4	0	—	13
6	4-	0	—	14
7	4	0	115	120
7	4-	0	—	42
8	4-	0	96	102
0	5	0	266	231
1	5	0	283	252
1	5-	0	67	76
2	5	0	285	263
2	5-	0	243	233
3	5	0	195	175
3	5-	0	162	142
4	5	0	—	52
4	5-	0	64	71
5	5	0	117	105
5	5-	0	77	86
6	5	0	61	67
6	5-	0	41	54
7	5	0	—	73
7	5-	0	89	85
8	5-	0	—	52
0	6	0	120	100
1	6	0	133	122
1	6-	0	188	164
2	6	0	163	143
2	6-	0	117	112
3	6	0	249	219
3	6-	0	47	30-
4	6	0	78	76
4	6-	0	153	139
5	6	0	46	58
5	6-	0	177	180
6	6	0	104	115
6	6-	0	93	105
7	6-	0	—	34
0	7	0	117	116
1	7	0	120	108
1	7-	0	154	138
2	7	0	—	28
2	7-	0	40	49
3	7	0	74	75
3	7-	0	97	100
4	7	0	126	125
4	7-	0	186	176
5	7	0	65	69
5	7-	0	131	123
6	7-	0	100	103
7	7-	0	—	49
0	8	0	97	92
1	8	0	97	66
1	8-	0	187	170
2	8	0	86	89
2	8-	0	137	132
3	8	0	—	35
3	8-	0	112	106
4	8	0	58	67
4	8-	0	98	58
5	8	0	—	61
5	8-	0	100	100
6	8-	0	95	100
0	9	0	116	105
1	9	0	—	51
1	9-	0	126	122
2	9	0	89	96
2	9-	0	118	118
3	9	0	—	80
3	9-	0	86	62
4	9	0	—	47
4	9-	0	—	8
5	9-	0	55	55
0	10	0	34	43
1	10	0	—	35
1	10-	0	76	75
2	10	0	64	79
2	10-	0	93	94
3	10-	0	—	15
4	10-	0	—	7
1	11-	0	—	29
0	0	1	244	372
1	0	1	30	4-
1-	0	1	270	376
2	0	1	202	198
2-	0	1	361	470
3	0	1	240	244
3-	0	1	266	274
4	0	1	90	92
4-	0	1	130	137
5	0	1	125	103
5-	0	1	166	166
6	0	1	67	54
6-	0	1	56	54
7	0	1	125	114
7-	0	1	111	112
8	0	1	78	91
8-	0	1	52	71
0	1	1	228	289
0	1-	1	47	43
1	1	1	401	590
1-	1	1	85	55-
1	1-	1	38	53
1-	1-	1	218	240
2	1	1	254	299
2-	1	1	318	387
2	1-	1	260	302
2-	1-	1	347	394
3	1	1	228	224
3-	1	1	262	296
3	1-	1	46	59
3-	1-	1	347	351
4	1	1	111	100
4-	1	1	164	161
4	1-	1	147	146
4-	1-	1	—	40
5	1	1	168	166
5-	1	1	60	44-
5	1-	1	203	187
5-	1-	1	189	183
6	1	1	70	72
6-	1	1	54	50
6	1-	1	171	152
6-	1-	1	206	217
7	1	1	—	17
7-	1	1	195	188
7	1-	1	129	110
7-	1-	1	119	115
8	1	1	81	90
8-	1	1	70	80
8	1-	1	31	37
8-	1-	1	20	41
0	2	1	120	70-
0	2-	1	61	66
1	2	1	381	453
1-	2	1	67	108
1	2-	1	249	282
1-	2-	1	264	249
2	2	1	373	384
2-	2	1	208	198
2	2-	1	231	228
2-	2-	1	92	96
3	2	1	224	229
3-	2	1	172	171
3	2-	1	131	138
3-	2-	1	178	166
4	2	1	122	114
4-	2	1	152	159
4	2-	1	277	273
4-	2-	1	117	111
5	2	1	130	128
5-	2	1	55	45
5	2-	1	208	188
5-	2-	1	113	119
6	2	1	203	190
6-	2	1	173	155
6	2-	1	207	186
6-	2-	1	222	219
7	2	1	60	54
7-	2	1	122	122
7	2-	1	76	61
7-	2-	1	108	110
8-	2	1	97	93
8	2-	1	—	21
8-	2-	1	—	60
0	3	1	139	139
0	3-	1	205	196
1	3	1	267	241
1-	3	1	86	93
1	3-	1	497	518
1-	3-	1	169	169
2	3	1	207	211
2-	3	1	33	4-
2	3-	1	242	236
2-	3-	1	195	186
3	3	1	62	61
3-	3	1	297	310
3	3-	1	191	193
3-	3-	1	46	61
4	3	1	176	173
4-	3	1	252	256
4	3-	1	159	143
4-	3-	1	138	134
5	3	1	136	130
5-	3	1	154	152
5	3-	1	163	159
5-	3-	1	69	67
6	3	1	153	143
6-	3	1	128	125
6	3-	1	159	150
6-	3-	1	138	127
7	3	1	108	104
7-	3	1	88	84
7	3-	1	—	25
7-	3-	1	89	86
8-	3	1	102	117
8	3-	1	33	32
0	4	1	330	336
0	4-	1	351	321
1	4	1	172	171
1-	4	1	168	152
1	4-	1	265	229
1-	4-	1	215	208
2	4	1	138	112
2-	4	1	125	131
2	4-	1	199	191
2-	4-	1	248	242
3	4	1	—	0
3-	4	1	294	279
3	4-	1	227	216
3-	4-	1	98	90
4	4	1	103	105
4-	4	1	203	212
4	4-	1	—	26
4-	4-	1	159	159
5	4	1	159	156
5-	4	1	199	183
5	4-	1	80	64
5-	4-	1	140	143
6	4	1	75	76
6-	4	1	68	60
6	4-	1	115	98
6-	4-	1	41	40
7	4	1	69	72
7-	4	1	63	60
7	4-	1	109	109
7-	4-	1	37	42
8-	4	1	78	74
8	4-	1	—	52
0	5	1	358	361
0	5-	1	63	65
1	5	1	260	244
1-	5	1	129	123
1	5-	1	104	85
1-	5-	1	127	131
2	5	1	103	72
2-	5	1	169	151
2	5-	1	325	289
2-	5-	1	299	284
3	5	1	55	61
3-	5	1	177	177
3	5-	1	103	93
3-	5-	1	219	215
4	5	1	88	99
4-	5	1	145	152
4	5-	1	58	37-
4-	5-	1	86	70
5	5	1	166	158
5-	5	1	83	74
5	5-	1	116	93
5-	5-	1	146	139
6	5	1	41	42
6-	5	1	—	26
6	5-	1	162	151
6-	5-	1	79	93
7-	5	1	97	99
7	5-	1	135	133
0	6	1	162	143
0	6-	1	66	66
1	6	1	199	179
1-	6	1	175	155
1	6-	1	81	85
1-	6-	1	88	89
2	6	1	134	117
2-	6	1	164	159
2	6-	1	182	165
2-	6-	1	84	85
3	6	1	156	148
3-	6	1	—	28
3	6-	1	105	110
3-	6-	1	209	197
4	6	1	94	105
4-	6	1	58	57
4	6-	1	166	154
4-	6-	1	111	103
5	6	1	110	99
5-	6	1	70	69
5	6-	1	116	95
5-	6-	1	71	71
6	6	1	54	66
6-	6	1	109	107
6	6-	1	95	87
6-	6-	1	67	84
7-	6	1	76	83
7	6-	1	106	111
0	7	1	117	107
0	7-	1	61	41
1	7	1	76	64
1-	7	1	162	149
1	7-	1	92	75
1-	7-	1	159	180
2	7	1	—	41
2-	7	1	—	27
2	7-	1	150	159
2-	7-	1	104	97
3	7	1	140	135
3-	7	1	57	60
3	7-	1	228	215
3-	7-	1	49	40
4	7	1	159	162
4-	7	1	153	142
4	7-	1	153	141
4-	7-	1	61	59
5	7	1	44	50
5-	7	1	95	91
5	7-	1	—	24
5-	7-	1	40	59
6-	7	1	78	72
6	7-	1	84	76
7-	7	1	—	72
0	8	1	79	76
0	8-	1	106	106
1	8	1	95	73
1-	8	1	84	69
1	8-	1	104	100
1-	8-	1	152	147
2	8	1	67	67
2-	8	1	90	85
2	8-	1	94	89
2-	8-	1	150	135
3	8	1	—	41
3-	8	1	169	164
3	8-	1	157	152
3-	8-	1	—	23
4	8	1	89	94
4-	8	1	111	104
4	8-	1	83	80
4-	8-	1	38	36
5-	8	1	49	59
5	8-	1	—	32
6-	8	1	54	62
6	8-	1	34	32
0	9	1	90	88
0	9-	1	100	102
1	9	1	47	60
1-	9	1	84	84
1	9-	1	51	41
1-	9-	1	116	114
2	9	1	46	81
2-	9	1	128	101
2	9-	1	51	56
2-	9-	1	116	117
3	9	1	49	56
3-	9	1	98	99
3	9-	1	84	75
3-	9-	1	43	41
4-	9	1	74	77
4	9-	1	—	32
5-	9	1	52	65
5	9-	1	33	47
0	10	1	69	82
0	10-	1	77	91
1	10	1	59	74
1-	10	1	57	58
1	10-	1	43	43
1-	10-	1	46	54
2	10	1	—	62
2-	10	1	37	57
2	10-	1	—	21
2-	10-	1	—	29
3-	10	1	29	39
3	10-	1	—	18
4-	10	1	—	54
4	10-	1	—	77
0	0	2	119	191
1	0	2	26	31
1-	0	2	168	198
2	0	2	189	216
2-	0	2	253	294
3	0	2	211	211
3-	0	2	149	155
4	0	2	46	27
4-	0	2	184	183
5	0	2	76	72
5-	0	2	259	258
6	0	2	125	119
6-	0	2	91	82
7	0	2	162	161
7-	0	2	42	35
0	1	2	285	377
0	1-	2	55	81
1	1	2	254	289
1-	1	2	198	262
1	1-	2	31	35
1-	1-	2	120	124
2	1	2	65	72
2-	1	2	184	212
2	1-	2	268	288
2-	1-	2	127	126
3	1	2	170	167
3-	1	2	106	117
3	1-	2	204	202
3-	1-	2	229	237
4	1	2	102	88
4-	1	2	235	246
4	1-	2	166	162
4-	1-	2	136	116
5	1	2	84	76
5-	1	2	134	132
5	1-	2	122	97
5-	1-	2	177	172
6	1	2	78	79
6-	1	2	39	36
6	1-	2	125	111
6-	1-	2	123	121
7	1	2	79	79
7-	1	2	52	49
7	1-	2	146	147
7-	1-	2	84	85
0	2	2	132	145
0	2-	2	64	82
1	2	2	309	343
1-	2	2	234	240
1	2-	2	150	173
1-	2-	2	268	270
2	2	2	222	229
2-	2	2	192	211
2	2-	2	281	272
2-	2-	2	116	113
3	2	2	153	133
3-	2	2	65	78
3	2-	2	273	255
3-	2-	2	135	126
4	2	2	118	109
4-	2	2	66	60
4	2-	2	235	221
4-	2-	2	98	91
5	2	2	121	113
5-	2	2	80	77
5	2-	2	69	59
5-	2-	2	83	70
6	2	2	145	131
6-	2	2	178	174
6	2-	2	86	72
6-	2-	2	125	122
7	2	2	30	26
7-	2	2	59	65
7	2-	2	84	79
7-	2-	2	64	75
0	3	2	96	97
0	3-	2	274	261
1	3	2	53	62
1-	3	2	269	277
1	3-	2	202	204
1-	3-	2	336	322
2	3	2	205	192
2-	3	2	96	111
2	3-	2	64	64
2-	3-	2	200	183
3	3	2	206	187
3-	3	2	49	55
3	3-	2	250	232
3-	3-	2	88	79
4	3	2	182	164
4-	3	2	58	47
4	3-	2	208	209
4-	3-	2	159	154
5	3	2	82	82
5-	3	2	189	175
5	3-	2	54	37
5-	3-	2	67	53
6	3	2	109	109
6-	3	2	196	188
6	3-	2	—	8
6-	3-	2	67	64
7	3	2	69	81
7-	3	2	50	63
7	3-	2	50	48
7-	3-	2	58	62
0	4	2	122	114
0	4-	2	255	231
1	4	2	—	13
1-	4	2	169	152
1	4-	2	—	34
1-	4-	2	318	303
2	4	2	124	130
2-	4	2	191	201
2	4-	2	45	42
2-	4-	2	258	248
3	4	2	135	129
3-	4	2	176	180
3	4-	2	229	200
3-	4-	2	56	29
4	4	2	129	124
4-	4	2	81	74
4	4-	2	95	90
4-	4-	2	127	129
5	4	2	94	98
5-	4	2	163	159
5	4-	2	65	62
5-	4-	2	160	171
6	4	2	60	57
6-	4	2	149	140
6	4-	2	61	59
6-	4-	2	71	78
7-	4	2	93	101
7	4-	2	82	84
0	5	2	133	126
0	5-	2	207	186
1	5	2	90	93
1-	5	2	141	142
1	5-	2	99	94
1-	5-	2	90	74
2	5	2	126	119
2-	5	2	251	234
2	5-	2	75	77
2-	5-	2	128	111
3	5	2	130	124
3-	5	2	167	168
3	5-	2	60	48
3-	5-	2	152	137
4	5	2	56	50
4-	5	2	88	100
4	5-	2	140	129
4-	5-	2	104	100
5	5	2	64	67
5-	5	2	80	75
5	5-	2	195	185
5-	5-	2	146	146
6	5	2	36	47
6-	5	2	65	65
6	5-	2	64	73
6-	5-	2	73	89
7-	5	2	78	94
7	5-	2	50	57
0	6	2	64	58
0	6-	2	215	193
1	6	2	191	184
1-	6	2	92	93
1	6-	2	113	113
1-	6-	2	129	112
2	6	2	171	170
2-	6	2	218	205
2	6-	2	97	88
2-	6-	2	69	44-
3	6	2	115	101
3-	6	2	140	143
3	6-	2	104	93
3-	6-	2	89	83
4	6	2	—	20
4-	6	2	52	50
4	6-	2	203	186
4-	6-	2	118	127
5	6	2	48	46
5-	6	2	—	4-
5	6-	2	123	118
5-	6-	2	103	113
6-	6	2	70	76
6	6-	2	49	53
0	7	2	45	44
0	7-	2	135	124
1	7	2	105	107
1-	7	2	98	101
1	7-	2	188	180
1-	7-	2	121	110
2	7	2	146	147
2-	7	2	80	77
2	7-	2	131	122
2-	7-	2	45	35
3	7	2	107	105
3-	7	2	73	58
3	7-	2	87	87
3-	7-	2	64	69
4	7	2	43	46
4-	7	2	62	65
4	7-	2	104	96
4-	7-	2	91	103
5	7	2	—	28
5-	7	2	53	67
5	7-	2	56	54
5-	7-	2	—	51
6-	7	2	54	74
6	7-	2	58	55
0	8	2	70	83
0	8-	2	106	101
1	8	2	98	98
1-	8	2	—	22
1	8-	2	134	121
1-	8-	2	98	86
2	8	2	62	67
2-	8	2	—	19
2	8-	2	66	63
2-	8-	2	91	98
3	8	2	—	25
3-	8	2	107	118
3	8-	2	79	79
3-	8-	2	69	84
4	8	2	—	64
4-	8	2	90	104
4	8-	2	39	38
4-	8-	2	—	100
5-	8	2	43	61
5	8-	2	—	27
0	9	2	54	68
0	9-	2	48	53
1	9	2	68	75
1-	9	2	40	41
1	9-	2	74	72
1-	9-	2	—	21
2	9	2	54	99
2-	9	2	75	85
2	9-	2	55	96
2-	9-	2	76	100
3-	9	2	81	94
3	9-	2	39	36
4-	9	2	43	57
4	9-	2	—	33
0	10	2	—	73
0	10-	2	—	73
1-	10	2	44	66
1	10-	2	—	28
2-	10	2	—	69
2	10-	2	—	27
0	0	3	160	194
1	0	3	74	90
1-	0	3	96	108
2	0	3	61	61
2-	0	3	140	131
3	0	3	110	91
3-	0	3	124	102
4	0	3	137	128
4-	0	3	141	129
5	0	3	153	157
5-	0	3	193	174
6	0	3	63	71
6-	0	3	112	101
7-	0	3	—	93
0	1	3	161	213
0	1-	3	201	216
1	1	3	79	78
1-	1	3	219	233
1	1-	3	160	180
1-	1-	3	84	91
2	1	3	27	15-
2-	1	3	164	172

Table 3 (*cont.*)

h	k	l	$10F_o$	$10F_c$
2	1-	3	164	160
2-	1-	3	18	15
3	1	3	154	139
3-	1	3	105	84
3	1-	3	70	73
3-	1-	3	135	120
4	1	3	166	146
4-	1	3	211	196
4	1-	3	146	145
4-	1-	3	110	103
5	1	3	82	80
5-	1	3	143	129
5	1-	3	164	160
5-	1-	3	137	125
6	1	3	23	25
6-	1	3	58	54
6	1-	3	67	79
6-	1-	3	80	78
7-	1	3	—	62
7	1-	3	—	36
0	2	3	198	175
0	2-	3	227	212
1	2	3	234	204
1-	2	3	200	182
1	2-	3	308	304
1-	2-	3	121	107
2	2	3	91	78
2-	2	3	151	141
2	2-	3	164	163
2-	2-	3	35	35
3	2	3	100	97
3-	2	3	184	164
3	2-	3	30	26
3-	2-	3	178	179
4	2	3	159	147
4-	2	3	136	122
4	2-	3	131	120
4-	2-	3	140	133
5	2	3	76	69
5-	2	3	—	4
5	2-	3	106	115
5-	2-	3	36	32
6	2	3	17	16
6-	2	3	56	58
6	2-	3	53	66
6-	2-	3	42	43
7-	2	3	—	82
7	2-	3	—	20
0	3	3	90	86
0	3-	3	193	163
1	3	3	130	105
1-	3	3	190	160
1	3-	3	206	200
1-	3-	3	166	146
2	3	3	218	194
2-	3	3	130	114
2	3-	3	81	83
2-	3-	3	120	113
3	3	3	159	152
3-	3	3	103	96
3	3-	3	95	95
3-	3-	3	160	150
4	3	3	114	104
4-	3	3	53	45
4	3-	3	74	73
4-	3-	3	209	198
5	3	3	39	40
5-	3	3	87	78
5	3-	3	34	39
5-	3-	3	50	51
6	3	3	41	50
6-	3	3	79	82
6	3-	3	52	69
6-	3-	3	—	21
0	4	3	139	132
0	4-	3	35	30
1	4	3	61	61
1-	4	3	97	79
1	4-	3	132	119
1-	4-	3	54	42
2	4	3	107	104
2-	4	3	46	42
2	4-	3	132	135
2-	4-	3	245	216
3	4	3	136	132
3-	4	3	109	102
3	4-	3	95	95
3-	4-	3	178	157
4	4	3	112	101
4-	4	3	148	133
4	4-	3	18	17
4-	4-	3	117	103
5	4	3	44	46
5-	4	3	140	131
5	4-	3	78	94
5-	4-	3	59	66
6-	4	3	34	42
6	4-	3	70	107
0	5	3	142	124
0	5-	3	106	94
1	5	3	92	83
1-	5	3	80	77
1	5-	3	113	101
1-	5-	3	16	6
2	5	3	54	55
2-	5	3	104	91
2	5-	3	107	113
2-	5-	3	106	100
3	5	3	69	72
3-	5	3	115	104
3	5-	3	78	88
3-	5-	3	161	150
4	5	3	57	58
4-	5	3	156	151
4	5-	3	91	111
4-	5-	3	64	61
5	5	3	49	62
5-	5	3	119	126
5	5-	3	93	127
5-	5-	3	29	42
6-	5	3	30	42
6	5-	3	26	50
0	6	3	136	123
0	6-	3	99	97
1	6	3	116	115
1-	6	3	123	109
1	6-	3	85	88
1-	6-	3	110	114
2	6	3	47	48
2-	5	3	54	89
2	6-	3	113	133
2-	6-	3	72	75
3	6	3	44	47
3-	6	3	76	76
3	6-	3	81	99
3-	6-	3	70	79
4	6	3	33	45
4-	6	3	105	111
4	6-	3	78	105
4-	6-	3	10	18
5-	6	3	64	72
5	6-	3	44	72
0	7	3	78	79
0	7-	3	80	93
1	7	3	65	68
1-	7	3	126	133
1	7-	3	94	109
1-	7-	3	119	137
2	7	3	60	[illegible]
2-	7	3	68	[illegible]
2	7-	3	59	[illegible]
2-	7-	3	72	[illegible]
3	7	3	60	[illegible]
3-	7	3	—	[illegible]
3	7-	3	33	49
3-	7-	3	49	[illegible]
4-	7	3	23	27
4	7-	3	42	[illegible]
5-	7	3	—	73
5	7-	3	—	[illegible]
0	8	3	[illegible]	72
0	8-	3	[illegible]	[illegible]
1	[illegible]	3	—	[illegible]
1-	[illegible]	3	39	[illegible]
1	[illegible]	3	40	[illegible]
1-	[illegible]	3	[illegible]	[illegible]
2	[illegible]	3	[illegible]	[illegible]
2-	[illegible]	3	—	[illegible]
2	[illegible]	3	[illegible]	[illegible]
2-	[illegible]	3	[illegible]	[illegible]
3-	[illegible]	3	—	[illegible]
3	[illegible]	3	[illegible]	[illegible]
4-	[illegible]	3	—	[illegible]
4	[illegible]	3	—	[illegible]
[illegible]	[illegible]	3	—	[illegible]
[illegible]	[illegible]	3	—	[illegible]
[illegible]	[illegible]	3	—	[illegible]
[illegible]	[illegible]	3	—	[illegible]
2-	[illegible]	3	—	[illegible]
2	[illegible]	3	—	[illegible]

Table 4. *Main interatomic distances and angles**

Hydrazine molecule:

N(1)–N(2)	=1·458±0·011 Å	H(4)–N(2)–H(3)	=124·7°
N(1)$_{\mathrm{III}}$′–H(1)	=1·47 Å	H(2)$_{\mathrm{III}}$′–N(1)$_{\mathrm{III}}$′–H(1)	=111·4
N(1)$_{\mathrm{III}}$′–H(2)$_{\mathrm{III}}$′	=1·03	Zn–N(2)$_{\mathrm{XI}}$′–N(1)$_{\mathrm{XI}}$′	=114·0±0·4
N(2)–H(3)	=1·17	Zn$_{\mathrm{VI}}$–N(1)$_{\mathrm{XI}}$′–N(2)$_{\mathrm{XI}}$′	=115·9±0·3
N(2)–H(4)	=0·98		

Coordination complex:

Zn$_{\mathrm{V}}$–N(1)$_{\mathrm{X}}$′	=2·179±0·007 Å	N(1)$_{\mathrm{III}}$′–O(1)$_{\mathrm{VII}}$	=3·194±0·010 Å
Zn$_{\mathrm{V}}$–N(2)$_{\mathrm{V}}$	=2·206±0·007	N(2)$_{\mathrm{IV}}$′–O(1)$_{\mathrm{VII}}$	=3·175±0·008
Zn$_{\mathrm{V}}$–O(1)$_{\mathrm{VII}}$	=2·147±0·005		
N(1)$_{\mathrm{X}}$–O(1)$_{\mathrm{VII}}$	=2·918±0·007	O(1)$_{\mathrm{II}}$–Zn–N(1)$_{\mathrm{VIII}}$′	=95·2±0·2°
N(2)$_{\mathrm{V}}$–O(1)$_{\mathrm{VII}}$	=2·979±0·009	O(1)$_{\mathrm{II}}$–Zn–N(2)$_{\mathrm{I}}$′	=93·7±0·2
N(1)$_{\mathrm{X}}$–N(2)$_{\mathrm{V}}$	=3·102±0·012	N(1)$_{\mathrm{VII}}$–Zn–N(2)	=90·0±0·3
N(1)$_{\mathrm{X}}$–N(2)$_{\mathrm{IV}}$′	=3·100±0·007	Zn–O(1)$_{\mathrm{II}}$–C(1)$_{\mathrm{II}}$	=129·7±0·5

Acetate group:

C(1)$_{\mathrm{VII}}$–O(1)$_{\mathrm{VII}}$	=1·264±0·007 Å	O(1)$_{\mathrm{II}}$–C(1)$_{\mathrm{II}}$–O(2)$_{\mathrm{XI}}$	=125·9±0·7°
C(1)$_{\mathrm{VII}}$–O(2)	=1·250±0·009	C(2)$_{\mathrm{II}}$–C(1)$_{\mathrm{II}}$–O(1)$_{\mathrm{II}}$	=116·2±0·7
C(1)$_{\mathrm{VII}}$–C(2)$_{\mathrm{VII}}$	=1·530±0·012	C(2)$_{\mathrm{II}}$–C(1)$_{\mathrm{II}}$–O(2)$_{\mathrm{XI}}$	=117·9±0·6
O(1)$_{\mathrm{VII}}$–O(2)	=2·239±0·007	C(1)$_{\mathrm{II}}$–C(2)$_{\mathrm{II}}$–H(5)$_{\mathrm{II}}$	=93·8°
C(2)$_{\mathrm{VII}}$–H(5)$_{\mathrm{VII}}$	=1·18 Å	C(1)$_{\mathrm{II}}$–C(2)$_{\mathrm{II}}$–H(6)$_{\mathrm{II}}$′	=121·2
C(2)$_{\mathrm{VII}}$–H(6)$_{\mathrm{VII}}$′	=1·29	C(1)$_{\mathrm{II}}$–C(2)$_{\mathrm{II}}$–H(7)$_{\mathrm{II}}$′	=94·7
C(2)$_{\mathrm{VII}}$–H(7)$_{\mathrm{VII}}$′	=1·16	H(5)$_{\mathrm{II}}$–C(2)$_{\mathrm{II}}$–H(6)$_{\mathrm{II}}$′	=138·0
		H(5)$_{\mathrm{II}}$–C(2)$_{\mathrm{II}}$–H(7)$_{\mathrm{II}}$′	=137·0
		H(6)$_{\mathrm{II}}$′–C(2)$_{\mathrm{II}}$–H(7)$_{\mathrm{II}}$′	=76·1

Intermolecular neighbours:

O(2)$_{\mathrm{IV}}$′ · · · N(1)$_{\mathrm{III}}$′	=2·988±0·009 Å	C(2)$_{\mathrm{VII}}$ · · · N(2)$_{\mathrm{VII}}$′	=3·534±0·011 Å
O(2)$_{\mathrm{IV}}$′ · · · N(2)$_{\mathrm{IV}}$′	=2·985±0·009	H(5)$_{\mathrm{VII}}$ · · · H(5)$_{\mathrm{VII}}$′	=2·14 Å
C(2)$_{\mathrm{VII}}$ · · · C(2)$_{\mathrm{VII}}$′	=4·033±0·014		
C(2)$_{\mathrm{VII}}$ · · · C(2)$_{\mathrm{V}}$′	=3·894±0·014	N(1)$_{\mathrm{III}}$′ · · · O(2)$_{\mathrm{IV}}$′ · · · N(2)$_{\mathrm{IV}}$′	=62·6±0·2°
C(2)$_{\mathrm{VII}}$ · · · C(1)$_{\mathrm{V}}$′	=4·070±0·011	O(2)$_{\mathrm{IV}}$′ · · · N(1)$_{\mathrm{III}}$′–H(2)$_{\mathrm{III}}$′	=14·3°
O(2)$_{\mathrm{IX}}$′ · · · N(1)$_{\mathrm{X}}$	=2·924±0·010	O(2)$_{\mathrm{IV}}$′ · · · N(2)$_{\mathrm{IV}}$′–H(3)$_{\mathrm{IV}}$′	=25·9

Asymmetric units† ($0 \le x \le 1$, $0 \le y \le 0{\cdot}5$, $0 \le z \le 1$)

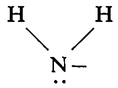
No label	x	y	z	VII	x	y	$-1+z$
I′	$-x$	$-y$	$-z$	VII′	$1-x$	$1-y$	$-z$
II	$-1+x$	y	$-1+z$	VIII′	$-x$	$-y$	$1-z$
II′	$-x$	$1-y$	$-z$	IX′	$2-x$	$-y$	$-z$
III	x	$-1+y$	z	X	$1+x$	y	$-1+z$
III′	$1-x$	$-y$	$1-z$	X′	$2-x$	$1-y$	$-z$
IV′	$1-x$	$-y$	$-z$	XI	$-1+x$	y	z
V	$1+x$	y	z	XI′	$-x$	$1-y$	$1-z$
V′	$2-x$	$1-y$	$1-z$	XII	$1+x$	$-1+y$	z
VI	x	y	$1+z$	XII′	$2-x$	$-y$	$1-z$

* Distances and angles involving hydrogen atoms are to be considered only as probable and approximate.

† Subscripts of asymmetric units make it possible to identify the atoms in the diagrams. The subscripts are omitted in the text.

(Nardelli, Fava & Giraldi, 1963), 2·12 Å (Iitaka, Oswald & Locchi, 1962), 2·16 Å (Nowacki & Silverman, 1961), 2·14 Å, 2·15 Å (Doyne & Pepinsky, 1957), 2·18 Å, 2·17 Å (Niekerk, Schoening & Talbot, 1953). The comparison shows how the bonds between zinc and nitrogen, in the present case, are the longest that have been found. Therefore that bond can be considered as a weak covalent bond or an ion-dipole bond. The Zn–O bond distance agrees very well with the other distances found in octahedral complexes of zinc. Following the arguments of Nowacki & Silverman (1961), who consider the bond Zn–O to be very likely electrovalent in octahedral complexes, the character of this bond can be regarded as electrovalent also in the present compound.

In the clinographic projection of part of the structure (Fig. 3), there appear clearly the chains of complexes. Two successive octahedra of the same chain are linked to one another by two bridges formed by hydrazine molecules. The distance between two nitrogen atoms of the same hydrazine molecule is N(1)–N(2) = 1·458 ± 0·011 Å, which agrees well with the averaged value 1·461 ± 0·009 Å (Ferrari, Braibanti, Bigliardi & Dallavalle, 1963) and with the value 1·45 Å found by Liminga & Olovsson (1964) at −165 °C. Hydrazine is in the staggered form. The azimuthal angle $\varphi = \pm 77{\cdot}6°$ can be found by projecting the bonds Zn–N(1) and Zn–N(2) on the plane normal to the line N(1)–N(2) (Fig. 4), by assuming that along the directions of the bonds Zn–N(1) and Zn–N(2) there are disposed the lone pairs of the two tetrahedral groups



(Ferrari, Braibanti & Bigliardi, 1963). When calculated from the projection of the bonds N–H on the plane normal to N(1)–N(2), the rotation is found to be 46° between H(1) and H(3), and 78° between H(2) and H(4) ($\varphi_{av} = 62°$). This result is satisfactory if it is taken into account that the hydrogen atoms can be located very roughly. The angle $\varphi = 62°$ is comparable to $\varphi = 58{\cdot}5°$ obtained by Liminga & Olovsson (1964). The two hydrazine molecules, facing each other, are enantiomorphous and can be distinguished as follows: *r*-form, if the rotation of the upper half molecule, from

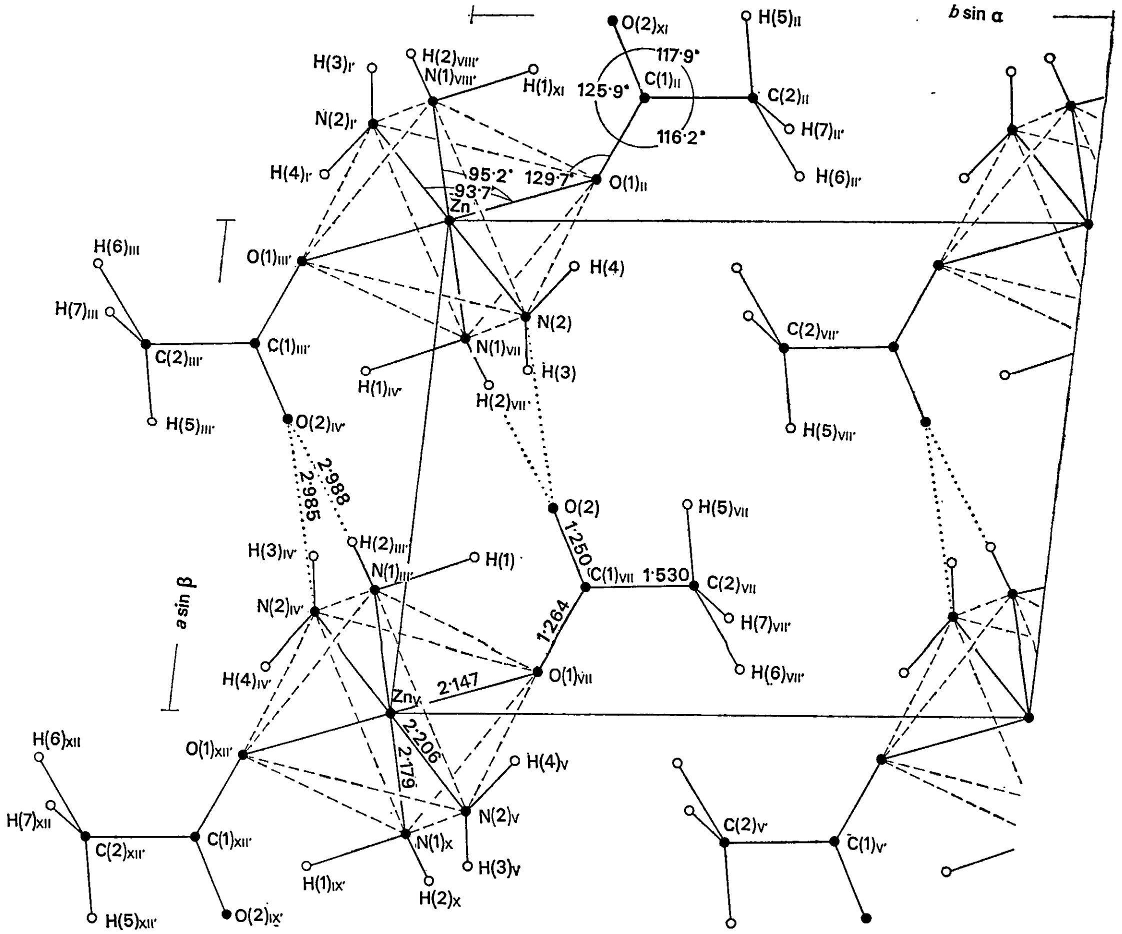


Fig. 2. One layer of the structure, parallel to (001), viewed down [001]. Only complexes with their centres at $z = 0$ are represented. Open circles indicate the probable positions of hydrogen atoms. Intermolecular hydrogen bonds are dotted.

the *cis*-position, is *right*-handed (φ positive); *l*-form, if the rotation of the upper half molecule, from the *cis*-position, is *left*-handed (φ negative).

The distances and angles indicate that the coordination octahedron is more distorted in this than in the other compounds of the type $[Zn(N_2H_4)_2]_nX_{2n}$ (Table 5). On the contrary, the rotation (azimuthal angle φ) between the two NH_2 groups forming the hydrazine molecule is practically constant in the different compounds; also the angles Zn · · · N(2)–N(1) = 114·0 ± 0·4° and Zn · · · N(1)–N(2) = 115·9 ± 0·3°, between the directions of the metal–nitrogen bonds and that of the nitrogen–nitrogen bond of hydrazine, are practically constant, irrespective of the anion and metal cation forming the complex. It seems that the bonds in hydrazine and formed by hydrazine are rather rigidly localized. The repeat distance along the chain (*i.e.* *c* of the unit cell) is equal for the acetate and chloride, but in the isothiocyanate, it is longer than in the other two. The lengthening of the repeat distance in the complex with the isothiocyanate group, with respect to the complexes with chlorine and the acetate group, is common to the structures of the complexes with Cd or Mn (Ferrari, Braibanti, Bigliardi & Lanfredi, 1963).

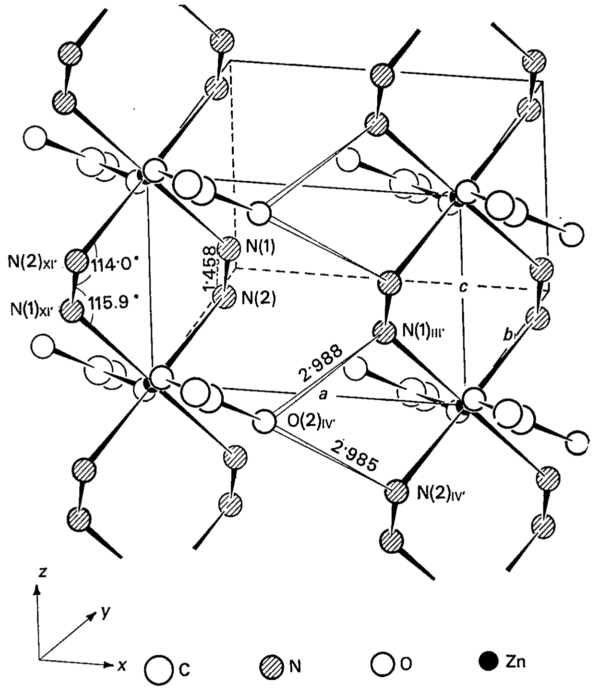


Fig. 3. Chains of complexes. Only chains along the lines [00*z*] and [10*z*] are drawn.

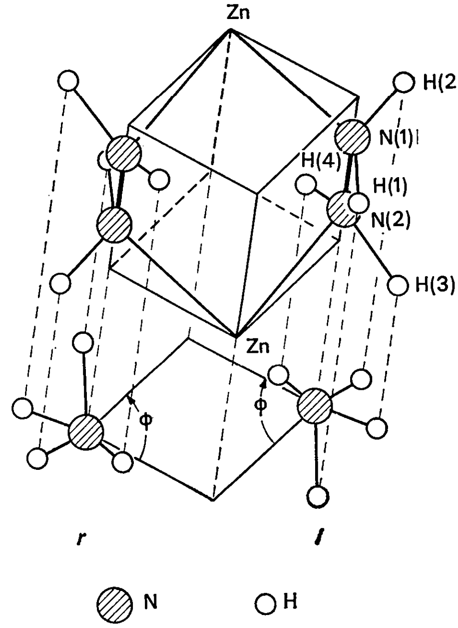
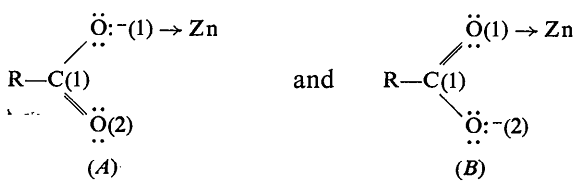


Fig. 4. Two enantiomorphous hydrazine molecules (*r*- and *l*-form). The azimuthal angle φ is obtained by projecting the bonds Zn–N on the plane normal to the bond N(1)–N(2).

Carboxylate group

In free carboxylic acids (Nardelli, Fava & Giraldi, 1962) the distance C–OH is greater than the distance C = O, and this difference has been interpreted by Pauling (1960) on the basis of the difference in single–double bond character of the two bonds. The predicted configuration for the carboxylate ion (Pauling, 1960) is that with the angle O–C–O = 125·27° and equal distances between carbon and oxygen. Our results, C(1)–O(1) = 1·264 ± 0·007 Å and C(1)–O(2) = 1·250 ± 0·009 Å, are in favour of an almost purely ionic form of the carboxylate group in the present compound, due to the resonance between the structures

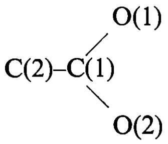


$$\text{R—C(1)}\begin{smallmatrix}\diagup\ddot{\underset{..}{\text{O}}}{:}^{-}\text{(1)}\rightarrow\text{Zn}\\ \diagdown\!\!\diagdown\ddot{\underset{..}{\text{O}}}\text{(2)}\end{smallmatrix}\quad\text{and}\quad\text{R—C(1)}\begin{smallmatrix}\diagup\!\!\diagup\ddot{\underset{..}{\text{O}}}\text{(1)}\rightarrow\text{Zn}\\ \diagdown\ddot{\underset{..}{\text{O}}}{:}^{-}\text{(2)}\end{smallmatrix}$$

(*A*) (*B*)

Not all the results, however, which have recently appeared confirm this point of view. In general, only when the environments of O(1) and O(2) are equal are the distances C(1)–O(1) and C(1)–O(2) equal or very close to each other: C(1)–O(1) = 1·248 Å, 1·250 Å, C(1)–O(2) = 1·236 Å, 1·250 Å (Hanic, Štempelová & Hanicová, 1964); C(1)–O(1) = 1·247 Å, 1·231 Å, C(1)–O(2) = 1·247 Å, 1·231 Å (Barclay & Kennard, 1961); C(1)–O(1) = 1·261 Å, C(1)–O(2) = 1·265 Å (Marsh, 1958). When, however, O(1) is bound to the metal and O(2) is bound through hydrogen bonds to other atoms, C(1)–O(1) is shorter than C(1)–O(2): *e.g.* C(1)–O(1) = 1·275 Å and C(1)–O(2) = 1·226 Å or C(1)–O(1) = 1·291 Å and C(1)–O(2) = 1·243 Å (Freeman, Snow, Nitta & Tomita, 1964); C(1)–O(1) = 1·311 Å and C(1)–O(2) = 1·206 Å (Freeman, Robinson & Schoone, 1964); C(1)–O(1) = 1·303 Å and C(1)–O(2) = 1·224 Å (Bryan, Poljak & Tomita, 1961); on the other hand, in the compound $Ni(NH_2CH_2CH_2COO)_2\,.\,2H_2O$ (Jose, Pant & Biswas, 1964), it has been observed that the distance C(1)–O(1)

(1·215 Å) is shorter than C(1)–O(2) (1·279 Å), although O(1) is bound to the metal and O(2) is not bound. The group



$$C(2){-}C(1)\begin{matrix}\diagup O(1)\\ \diagdown O(2)\end{matrix}$$

is planar. The plane is represented by: $1\cdot91353x+2\cdot72117y+3\cdot66530z-2\cdot85146=0$ (Schomaker, Waser, Marsh & Bergman, 1959). Deviations from planarity are well within the e.s.d.'s $[(\overline{\Delta d^2})^{\frac{1}{2}}=\pm0\cdot0003$ Å]. The angles O(1)–C(1)–O(2) = 125·9 ± 0·7°, C(2)–C(1)–O(1) = 116·2 ± 0·7° and C(2)–C(1)–O(2) = 117·9 ± 0·6° are regular with respect to the values obtained with other carboxylates. The angles O(1)–C(1)–O(2), C(2)–C(1)–O(1), C(2)–C(1)–O(2) have been found to be:

124·3°, 117·4°, 118·3° or
122·8°, 117·5°, 119·7° (Freeman, Snow, Nitta & Tomita, 1964);
127·8°, 115·7°, 116·4° or
123.3°, 118·9°, 117·2° (Hanic, Štempelová & Hanicová, 1964);
127·3°, 115·0°, 118·1° or
122·9°, — — (Barclay & Kennard, 1961);
122·7°, 120·9°, 116·9° (Bryan, Poljak & Tomita, 1961);
125·5°, 117·4°, 117·1° (Marsh, 1958).

In fact, O(1)–C(1)–O(2) is in general the greatest of the three, except in $C_6H_{10}N_3O_4$. CuCl . $1\frac{1}{2}H_2O$ where O(1)–C(1)–O(2) = 121·7° and C(2)–C(1)–O(2) = 125·5° (Freeman, Robinson & Schoone, 1964) and again in Ni $(NH_2CH_2CH_2COO)_2$. $2H_2O$ where O(1)–C(1)–O(2) = 122·7° and C(2)–C(1)–O(1) = 125·9° (Jose, Pant & Biswas, 1964). Also the distance C(1)–C(2) = 1·530 ± 0·012 Å is regular [C(1)–C(2) = 1·545 Å (Jose, Pant & Biswas, 1964); 1·498 Å, 1·541 Å (Freeman, Snow, Nitta & Tomita, 1964); 1·511 Å (Freeman, Robinson & Schoone, 1964); 1·525 Å, 1·549 Å (Hanic, Štempelová & Hanicová, 1964); 1·540 Å (Barclay & Kennard, 1961); 1·491 Å (Bryan, Poljak & Tomita, 1961); 1·523 Å (Marsh, 1958)], but sometimes the carbon–carbon distance, adjacent to a carboxylate group, is found to be significantly shortened [C(1)–C(2) = 1·467 Å (Barclay & Kennard, 1961)].

Interchain contacts

The shortest interchain distances are O(2) · · · N(1) = 2·988 ± 0·009 Å and O(2) · · · N(2) = 2·985 ± 0·009 Å (Fig. 5). These distances O · · · N can be considered as weak hydrogen bonds directed towards two nitrogen

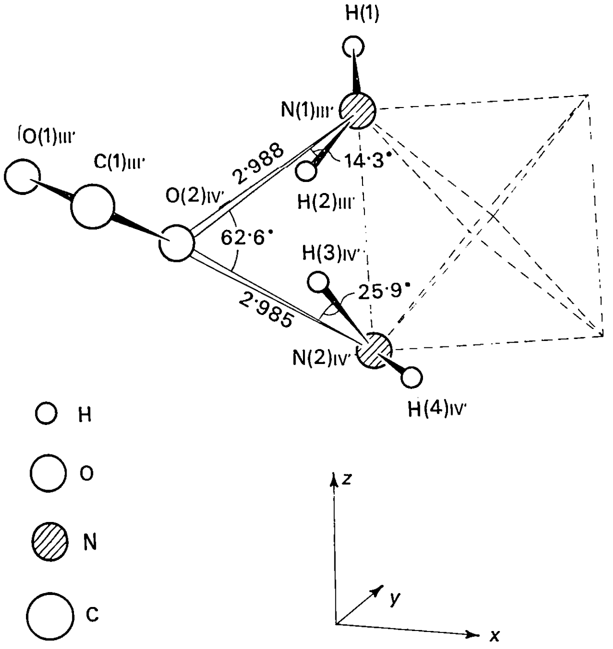
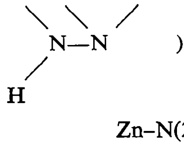


Fig. 5. Intermolecular hydrogen bonds between adjacent chains. The two chains involved are the same as in Fig. 5.

Table 5. *Comparison between corresponding distances and angles in the compounds* $[Zn(N_2H_4)_2]_nX_{2n}$

	X = Cl (*a*)	X = (NCS)* (*b*)	X = (CH₃COO)† (*c*)
N(1)–N(2) (hydrazine)	1·46 Å	1·47 Å	1·458 Å
Zn–N(1)	2·15	2·16	2·179
Zn–N(2)		2·18	2·206
Zn–X	2·578	2·19*	2·147†
c repeat distance	4·13	4·21	4·14
φ (rotation )	74°	74°	77·6°
Zn–N(2)–N(1)	117°	118°	114·0°
Zn–N(1)–N(2)			115·9°
X–Zn–N(1)	90°	89°*	95·2°†
X–Zn–N(2)			93·7°†

* Bound to the metal through nitrogen atom.
† Bound to the metal through oxygen atom.
(*a*) Ferrari, Braibanti & Bigliardi (1963).
(*b*) Ferrari, Braibanti, Bigliardi & Lanfredi (1965).
(*c*) Present work.

atoms of one octahedron in an adjacent chain. The atoms H(2) and H(3) are only slightly out of the line joining O(2) to N(1) and O(2) to N(2), respectively.

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Die Struktur des Natrium-hexametaphosphates $Na_6(P_6O_{18}) . 6H_2O$

VON K.-H. JOST

Institut für Anorganische Chemie der Deutschen Akademie der Wissenschaften zu Berlin, Berlin-Adlershof, Deutschland

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The structure of $Na_6(P_6O_{18}) . 6H_2O$, crystallizing in space group *Ccma* with unit-cell dimensions $a = 10{\cdot}58$, $b = 18{\cdot}54$, $c = 10{\cdot}48$ Å, was determined by direct methods. The anion $[P_6O_{18}]^{6-}$ forms a ring of six PO_4 tetrahedra which are connected at the corners.

Bis vor kurzem waren an Phosphaten mit ringförmigem Anion nur Tri- und Tetrametaphosphate bekannt. Von einigen dieser Verbindungen wurde die Struktur untersucht: $(NH_4)_4P_4O_{12}$ (Romers, Ketelaar & MacGillavry, 1951; Cruickshank, 1964), $LiK_2P_3O_9 . H_2O$ (Eanes & Ondik, 1962), $Na_3P_3O_9$ (Ondik, 1963), $Na_4P_4O_{12} . 4H_2O$ (Ondik, Block & MacGillavry, 1961; Ondik, 1964) und $Na_2H_2P_4O_{12}$ (Dornberger-Schiff, 1964; Jarchow, 1964). Auf Grund von Papierchromatogrammen vermuteten Van Wazer & Karl-Kroupa (1956), dass es auch höhere Metaphosphate gibt. Erstmals isoliert und chemisch eindeutig als Metaphosphate gekennzeichnet wurden diese Substanzen von Thilo & Schülke (1963), die aus Grahamschem Salz kristallisierte Penta- und Hexametaphosphate gewannen und papierchromatographisch auch Hepta- und Oktametaphosphat nachwiesen. In der vorliegenden Arbeit wurde das gegen hydrolytischen Angriff besonders beständige Hexametaphosphat in Form des Hydrates $Na_6P_6O_{18} . 6H_2O$ untersucht, dessen Anion also