

Crystal Structures of Complexes of Nickel Perchlorate with Substituted Pyridines. I. Bisperchloratotetrakis-(3,5-dimethylpyridine)nickel(II)*

BY FRANÇOISE MADAULE-AUBRY† AND GEORGE M. BROWN

Chemistry Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37830, U.S.A.

(Received 20 September 1967)

X-ray structure analysis shows that the blue solid $\text{Ni}(3,5\text{-dimethylpyridine})_4(\text{ClO}_4)_2$ is an octahedral complex compound in which the perchlorate ions are coordinated to the nickel ion, in agreement with the interpretation of spectroscopic and magnetic studies (Moore, Gayhart, & Bull, *J. Inorg. and Nuclear Chem.* (1964), **26**, 896; Buffagni, Vallarino & Quagliano, *Inorg. Chem.* (1964), **3**, 671). Crystals of the compound have the space-group symmetry $I4_1/acd$; $a=b=15.8759$ (17), $c=26.7581$ (25) Å, $Z=8$. Intensities of 1712 independent reflections (Cu $K\alpha$ radiation, $\sin \theta/\lambda \leq 0.639$) were recorded with the Oak Ridge computer-controlled diffractometer and were corrected for absorption. The structure was solved essentially from Patterson and Fourier syntheses as a heavy-atom problem. Disorder in the arrangement of the perchlorate group made the location of the three perchlorate oxygen atoms not coordinated to nickel rather difficult; these atoms were located eventually by use of the method of least-squares, the occupancy factors of closely spaced possible positions being adjusted to find the actual positions. Although the parameters of the remainder of the structure are fairly precisely determined, those of most of the atoms of the perchlorate group are not well determined because of the disorder; and the final value of the usual discrepancy index $R(F)$ has the rather high value 0.101. The nickel atom of the asymmetric unit is located at the point $0, \frac{1}{2}, \frac{1}{2}$ of the Wyckoff set (b) (point-group symmetry 222); the perchlorate group is in a disordered arrangement about the twofold axis $x, \frac{1}{2} + x, \frac{1}{2}$, which is perpendicular to the average plane of the nickel and nitrogen atoms defined by the twofold axes $x, \frac{1}{2} - x, \frac{1}{2}$ and $0, \frac{1}{2}, z$. The angle between the Ni-O bond and the twofold axis is 9.2° ; the Ni-O bond length is $2.187(4)^\circ$. The four organic ligands are in a propeller-like arrangement (pitch $\sim 47^\circ$) around the axis through the perchlorate. The Ni-N bond length is $2.093(2)$ Å. The nitrogen atoms are alternately 0.065 Å above and 0.065 Å below their average plane. The structure is very similar to that of $\text{Ni}(\text{pyridine})_4\text{Cl}_2$, which has the same space-group symmetry and nearly the same translations a and b (Porai-Koshits, *Structure Reports* (1954), **18**, 749).

Introduction

There has been considerable interest recently in the perchlorate ion with respect to its ability to act as a ligand in forming coordination compounds with metallic ions. Conductance, spectroscopic, and magnetic studies have been interpreted as indicating coordination of perchlorate to a variety of transition-metal ions. In two complex compounds of cobalt(II) the coordination of perchlorate has been authenticated by X-ray crystal-structure analysis: $\text{Co}(\text{CH}_3\text{SCH}_2\text{CH}_2\text{SCH}_3)_2(\text{ClO}_4)_2$ (Cotton & Weaver, 1965); $\text{Co}(\text{diphenylmethylarsine oxide})_4(\text{ClO}_4)_2$ (Pauling, Robertson & Rodley, 1965). One interesting series of compounds whose magnetic and spectral properties have been studied is the series $\text{Ni}(\text{py})_4(\text{ClO}_4)_2$, where py stands for pyridine and various substituted pyridines. The compounds studied fall into two classes:

(a) Blue compounds with magnetic moments about 3.25 Bohr magnetons: py = pyridine (Rosenthal &

Drago, 1965), 3,5-dimethylpyridine (Moore, Gayhart & Bull, 1964; Buffagni, Vallarino & Quagliano, 1964), 3-bromopyridine (Moore *et al.*, 1964), 4-isopropylpyridine (Moore *et al.*, 1964).

(b) Yellow diamagnetic compounds: py = 3,4-dimethylpyridine (Buffagni *et al.*, 1964), 4-methylpyridine (Moore *et al.*, 1964), 4-aminopyridine (Moore *et al.*, 1964).

Magnetic and spectral data have been interpreted as showing that the blue compounds are octahedral complexes with the perchlorate ions coordinated to nickel through oxygen and that the yellow compounds are square-planar complexes in which the perchlorate ions are not coordinated.

We have determined the crystal structure of $\text{Ni}(3,5\text{-dimethylpyridine})_4(\text{ClO}_4)_2$ and (with Dr W. R. Busing) that of $\text{Ni}(3,4\text{-dimethylpyridine})_4(\text{ClO}_4)_2$ to obtain direct evidence as to the role of the perchlorate ion and to discover the manner of arrangement of the substituted pyridine ligands in each case. Although the structure analysis for each compound was complicated by problems of disorder, our results show unambiguously that perchlorate ions are coordinated to nickel in the 3,5-dimethylpyridine compound and that they are not coordinated in the 3,4-dimethyl compound, in agree-

* Research sponsored by the U.S. Atomic Energy Commission under contract with the Union Carbide Corporation.

† Aided by a NATO postdoctoral fellowship. Present address: Centre de Recherche de Chimie, Ecole Centrale des Arts et Manufactures, 1 rue Montgolfer, 75, Paris III^e, France.

ment with the conclusions from magnetic and spectral data.

In this paper we report the structure of the 3,5-dimethylpyridine complex compound. Because our mode of handling the problems caused by disorder of the perchlorate ions may be of interest to others, we describe the procedure of structure analysis in some detail. In the following article (Madaule-Aubry, Busing & Brown, 1968) the structure of the 3,4-dimethylpyridine complex compound is presented.

Data

A sample of $\text{Ni}(\text{3,5-dimethylpyridine})_4(\text{ClO}_4)_2$ was given to us by Professor W. E. Bull of the University of Tennessee. Crystals were grown by evaporation from dichloromethane solution. The characteristic form of an isolated crystal is that of a tetragonal bipyramid. Usually the crystals are rather imperfect and aggregated. An apparently suitable specimen, roughly a cube 0.5 mm on an edge, was cut from a larger crystal and sealed inside a thin-walled glass tube for protection from the atmosphere.

From X-ray precession films approximate cell parameters were obtained; the space group $I4_1/acd$ was indicated by the systematic absences (*International Tables for X-ray Crystallography*, 1952, pp.247–248). The cell parameters, together with the orientational parameters of the crystal, were refined by the method of least-squares from angle data of 8 reflections ($\text{Cu } K\alpha_1$ radiation, wavelength 1.54051 Å assumed) determined with the Oak Ridge computer-controlled X-ray diffractometer (Busing, Ellison, Levy, King & Roseberry, 1968). The cell parameters established are $a=b=15.8759(17)$ Å and $c=26.7581(25)$ Å.*

The density of the compound was not determined accurately but was found to lie between that of chloroform, 1.498 g.cm⁻³, and dichloromethane, 1.336 g.cm⁻³. For 8 units $\text{Ni}(\text{C}_7\text{NH}_9)_4(\text{ClO}_4)_2$ of formula weight 686.2 in the cell volume of 6744.2 Å³ the calculated density is 1.351 g.cm⁻³. It was therefore assumed that there are 8 formula units per cell.

Intensity data were recorded with the automatic diffractometer using the θ - 2θ step-scan method and $\text{Cu } K\alpha$ radiation. The 2θ step width was 0.05°. The total width of scan for each reflection was 2° plus the width of the α_1 - α_2 doublet separation. For the 2θ range 0° to 95° the count time for each point in a scan was 2 seconds, and the time for the background counts taken at the beginning and end of each scan was 10 seconds; these count times were doubled for the 2θ range 95 to 159.6°. A nickel filter was used for reflections with 2θ below 95°; no filter was used for reflections at higher angles. The bisecting position of the χ circle ($\omega=0^\circ$)

* The numbers in parentheses corresponding to the least significant digits of the parameters are the standard errors from the least-squares refinement. We use this convention for indicating standard errors throughout the paper.

was used for the 2θ range up to 133.5° and the parallel position ($\chi=90^\circ$) for the 2θ range between 133.5° and 159.6°. A reference reflection (004 for the bisecting position and 0,0,32 for the parallel position) was recorded after every 20 reflections as a check on the stability of the instrument and the crystal. Exclusive of the measurements of the reference reflections, a total of 1956 observations were made of the intensities of 1712 independent reflections.

The quality of the intensity data is not so high as is normally attainable diffractometrically because the crystal specimen evidently contained one or more small volume elements misoriented with respect to the main body of material. This fact became apparent through the occasional appearance of a small satellite peak near the principal peak of a reflection. We estimate that the maximum error in peak intensity caused by a satellite is about 5%. Since no more promising crystal specimen was available, we decided to complete the data collection with the crystal in hand.

The raw data on punched paper tape were converted by calculations using the CDC 1604 computer to a set of structure-factor squares F_o^2 and standard errors $\sigma(F_o^2)$ on cards. The slight variations of intensity of each reference reflection were assumed to represent slowly varying instrumental conditions, and the reference intensities were used to normalize the data to a fixed standard value for each reference reflection. Absorption corrections calculated by the method of Busing & Levy (1957) were applied. The value of the absorption coefficient used was 26.9 cm⁻¹. The data for the parallel position were scaled to those of the bisecting position by use of the ratio of intensities of reflections 004 and 0,0,32 after correction for absorption. Different scale-factor identifiers were assigned to the groups of reflections in three ranges of 2θ as follows: (1) 0 to 95° (filtered radiation); (2) 95 to 133.5° (unfiltered radiation); (3) 133.5 to 159.6° (unfiltered radiation, parallel position). The value 5.6 Å² for the overall isotropic temperature factor and an approximate scale factor for the observations were obtained by the method of Wilson (1942).

Solution and refinement

Since there appeared to be 8 formula units $\text{Ni}(\text{3,5-dimethylpyridine})_4(\text{ClO}_4)_2$ in the cell, for which the general positions are 32-fold, it was clear that the nickel atoms must lie in one of the 2 sets of eightfold positions (point-group symmetry either 222 or $\bar{4}$) and that the chlorine atoms must lie on one of the 3 sets of twofold axes – if the structure is ordered with respect to the arrangement of these atoms.

Coefficients for a sharpened and modified three-dimensional Patterson synthesis (space group $I4/mmm$) were prepared by the method described by Donohue & Trueblood (1952). The most prominent peaks in the Patterson map are listed in Table 1. The principal interactions which were inferred to contribute to each

peak are shown in the last column of the table. All of these peaks are explained satisfactorily if one assumes that the nickel atoms are located on the 8 points of symmetry 222 of Wyckoff set (*b*) and that the chlorine atoms are located at 16 points of symmetry 2 of the Wyckoff set (*f*). The nickel atom and the chlorine atom of the asymmetric unit were taken to be at 0, 0.250, 0.125 and 0.155, 0.405, 0.125, respectively.* We presumed at this point that the perchlorate group occurs in the structure in twofold disorder, because on chemical grounds it seemed highly probable that one of the oxygen atoms would lie between Ni and Cl on the twofold axis, which could not then be a symmetry element for the perchlorate tetrahedron. The Patterson peaks representing the Ni-Cl interactions were elongated in the plane $z=0.25$ perpendicular to the twofold axis, suggesting that the chlorine atom might not be exactly on the axis.

Table 1. *The most prominent peaks in the three-dimensional Patterson map of Ni(3,5-dimethylpyridine)₄(ClO₄)₂*

The peak heights are on an arbitrary scale such that the peak at the origin has the height 999.

Peak	Height	Coordinates			Vectors
		<i>U</i>	<i>V</i>	<i>W</i>	
1	628	0.5	0	0.25	Ni-Ni and Cl-Cl
2	519	0.5	0.5	0	Ni-Ni
3	188	0.155	0.155	0	Ni-Cl
4	90	0.188	0.5	0	Cl-Cl

A three-dimensional Fourier synthesis was calculated for which the coefficients $|F_o|$ were phased by the signs of the structure-factor contributions of the nickel and chlorine atoms and weighted by the factor

$$w = \tanh \frac{|F_o| |F_c|}{\sum_j f_j^2 \exp(-2B \sin^2 \theta / \lambda^2)}$$

where f_j is the scattering factor for atom j at rest, and the summation is taken over all atoms in the cell except nickel and chlorine atoms (Woolfson, 1956). The nickel atoms in the Wyckoff positions (*b*) contribute only to one-fourth of the general reflections hkl , those for which $l=2n$ and $2k+l=4n$; and the chlorine atoms contribute only to one-half the general reflections, those for which $2k+l=2n+1$ or $4n$. Consequently, many of the observed structure factors could not be entered into the Fourier synthesis, and the map contained much false detail. Nevertheless, it was possible to pick out eight atoms in a configuration which roughly described the 3,5-dimethylpyridine ligand. Another peak located on the twofold axis between the nickel atom and the chlorine atom was tentatively identified as an oxygen atom. This peak was somewhat low in

height for an oxygen atom and somewhat elongated in the z direction.

A structure-factor calculation based on the nickel, chlorine, and carbon atoms gave a discrepancy index $R(F)=0.34$, to be compared with the value 0.52 that had been obtained when only the nickel and chlorine atoms were included. In the following Fourier synthesis the peak for the oxygen atom, O(1), on the twofold axis again appeared; but the six half-weight oxygen atoms representing in the disordered model the other three perchlorate oxygen atoms, O(2), O(3), and O(4), could not be placed in the smear of electron density found near the chlorine atom.

The problems of locating approximately the oxygen atoms O(2), O(3), and O(4) and of locating precisely the atoms O(1) and Cl originally placed on the twofold axis proved to be difficult. Several Fourier and difference syntheses, many cycles of least-squares refinement, and a number of bond-length and angle calculations were required to bring the structure determination to a reasonably satisfactory conclusion. A synopsis of the successive operations follows.

A series of least-squares refinement cycles was performed into which the atoms O(2), O(3), and O(4) were entered as 12 quarter-weight oxygen atoms equally spaced around a circle and in which the weights (occupancy factors) of the fractional oxygen atoms and the coordinates and isotropic temperature factors of the other atoms were adjusted. $R(F)$ dropped to 0.24, and the structure of the dimethylpyridine ligand became much more satisfactory. When anisotropic thermal parameters were used for all atoms except O(2), O(3), and O(4), the value of $R(F)$ fell to 0.20. Approximate positions for 6 half-oxygen atoms were deduced from the occupancy factors of the 12 quarter-weight positions. Atom O(1) was moved slightly from the twofold axis and represented as two half-atoms 180° apart around the axis, as suggested by analysis of its anisotropic thermal parameters. Least-squares refinement brought $R(F)$ down to 0.14. The three hydrogen atoms attached to the ring carbon atoms were located in a difference map, and the three hydrogen atoms of each methyl group were represented by 12 quarter-weight atoms on a circle. The chlorine atom was moved slightly from the twofold axis and represented by two half atoms. Adjustment of the occupancy factors of the fractional hydrogen atoms, the coordinates of the ring hydrogen atoms, and the coordinates and the anisotropic thermal parameters of the other atoms lowered $R(F)$ to 0.122. The hydrogen atoms of each methyl group were individually located from a difference map, and the coordinates and isotropic thermal parameters of all the hydrogen atoms were subsequently included among the parameters refined. The scattering factor curve for nickel was corrected for anomalous dispersion at this stage (through oversight this correction had not been made earlier). $R(F)$ became 0.099; $R(F^2)$, 0.087; R_w , 0.1089; σ_1 , 1.70. Finally the six reflections of highest intensity, judged as a group to be affected

* All coordinates quoted in this paper are referred to the origin at $\bar{1}$ (*International Tables*, 1952, p.248).

Table 2 (cont.)

L	OBS	CALC	SG	L	OBS	CALC	SG	L	OBS	CALC	SG	L	OBS	CALC	SG	L	OBS	CALC	SG	L	OBS	CALC	SG	L	OBS	CALC	SG	L	OBS	CALC	SG	L	OBS	CALC	SG	L	OBS	CALC	SG
*** 14	5	L	***	11 185	-211 38	21 114	-71 19	15W	0	5 19	21 153	115 16	3 96	-101 23	*** 11	8	L	***	4 157	-148 14	15W	67	18 46	*** 11	10	L	***	*** 17	10	L	***	16 67	57 19						
5 199	243 17	13W	0	5 5811 10	23W	46	62 38	23W	0	8 38	23W	0	5 78	53 30	*** 11	15	L	***	1 159	115 19	17W	38	-84 42	*** 11	13	L	***	11 31	71 26										
7M	0	-27 58	15	206	-475 16	*** 12	6	L	***	*** 18	6	L	***	9 68	10 27	3M	71	-127 64	8 125	100 16	19 69	-48 26	3 93	142 34	*** 3	6	L	***	*** 13	12	L	***	3 66	27 18					
9M	32	-78 59	17	412	-114 11	*** 12	6	L	***	0 154	-149 11	27 69	33 13	5 341	-167 64	10M	0	-15 36	21W	41	-5 24	5 190	-144 15	5W	0	3 22	1 115	73 20											
11 214	-213 14	19 85	-23 35	0 661	-680 12	3W	42	48 29	*** 11	7	L	***	11 79	-102 23	7 394	413 11	12 138	-139 11	23W	0	-23 16	7 234	212 14	7 66	46 14	3 72	57 30												
13M	67	33 53	21 108	-51 28	2W	76	127 64	4W	53	62 28	*** 11	7	L	***	15W	0	17 24	9W	0	11 63	14W	39	-67 23	9 146	157 21	5W	37	14 32											
15W	53	36 48	23M	67	9 55	4 244	260 14	6W	44	19 25	2 384	410 11	17W	0	-1 18	13 219	-209 16	*** 13	9	L	***	11 117	-174 25	*** 11	11	L	***	*** 11	11	L	***	7W	53	-6 39					
17W	0	6 43	25 101	7 22	6 191	177 16	8 88	-104 15	4 153	-132 19	*** 17	7	L	***	15 103	-43 27	*** 17	8	L	***	4 145	-128 20	15 64	62 30	2 133	71 21	9W	56	-75 38										
19 118	-113 15	27 119	90 16	8 450	-449 11	10W	0	-14 22	6 168	-189 19	8 130	-132 25	2 73	103 27	7 204	196 15	11 29	49 16	6 218	211 14	17W	0	-40 44	10 165	169 16	11W	0	5 64											
23W	0	30 18	29 94	88 14	10W	0	-21 65	12 475	460 8	12 161	156 20	4W	0	-51 37	19 168	-159 14	9W	0	-3 35	8 121	-67 29	9 62	92 30	14 127	-116 18	15W	19	13 21											
*** 15	5	L	***	*** 8	6	L	***	*** 19	6	L	***	12W	45	-18 61	6W	31	-45 36	21W	0	31 28	5 59	-30 26	10 153	-159 18	21W	41	-4 24	18 89	58 20										
2 366	-348 11	0 1059	-1072 17	16 251	-218 13	*** 19	6	L	***	1W	0	4 21	14 290	-253 12	8W	49	-4 26	23W	0	1 37	7W	0	-22 79	12W	22	21 48	23W	0	20 18										
4 114	86 24	2 215	176 21	18W	51	-44 52	3W	39	43 21	16W	34	13 57	10 133	110 10	12W	13	11 24	25 46	51 20	9W	0	3 27	14 126	99 18	11W	0	1 23	16W	51	-47 37									
6 349	345 10	4 600	585 13	20 244	235 11	5W	43	-44 19	20 106	54 21	14 67	-23 14	*** 12	8	L	***	0 486	493 11	*** 18	8	L	***	20W	0	8 22	2 175	-147 17												
8 139	-322 10	8 347	-324 16	*** 13	6	L	***	*** 7	7	L	***	2 1475	1460 23	26 56	37 16	*** 18	7	L	***	2W	65	64 61	0 84	73 14	*** 14	9	L	***	4 275	245 17									
12 105	51 21	10 69	-1010 65	*** 12	7	L	***	10 998	988 17	*** 12	7	L	***	3W	23	4 25	6 160	-39 20	4 114	-126 10	1W	0	6 353	8 215	-11 14	11 207	-204 12	12 139	-137 9										
14 208	206 17	12 633	660 14	1 186	-197 18	6 819	-958 15	14 891	-901 15	1 123	95 25	5W	0	-15 25	8 607	649 12	6 135	23 20	3 129	124 20	10W	0	4 753	13 128	126 10	14W	39	-30 17											
16 96	-47 19	14W	0	-110 64	3W	0	49 61	17 109	-46 27	3 243	258 14	7W	0	-23 23	10 118	-103 25	8 6W	5	179	-175 10	5 179	-125 15	7 108	94 23	15 15	65 41 29													
*** 16	5	L	***	16 503	-493 11	5W	0	-14 62	22 357	-353 11	5 139	-105 22	9W	0	-40 20	12 214	-207 14	14W	0	8 55	9 92	44 24	16 86	-69 23	19W	40	-32 27	1 82	-61 17										
1W	61	-27 49	20 394	376 11	9 87	-80 25	22 357	-353 11	5 139	-105 22	9W	0	-40 20	12 214	-207 14	14W	0	8 55	9 92	44 24	16 86	-69 23	19W	40	-32 27	1 82	-61 17												
3W	0	24 50	22 104	-43 27	11 198	150 16	26 231	239 10	9 202	186 17	*** 19	7	L	***	16 349	338 10	2 960	-1008 16	11 143	143 16	18W	21	6 34	*** 13	11	L	***	3W	27	-20 27									
5W	0	55 50	24 208	-275 13	13 79	119 38	*** 8	7	L	***	11 227	218 15	2 78	78 11	18W	53	-73 43	6 526	544 11	13 179	-119 16	20W	47	-21 23	*** 13	11	L	***	5 34	316 11									
7 120	-70 19	26 72	-35 15	35W	37	40 52	*** 8	7	L	***	1 671	-681 13	13 118	-53 34	20 130	-61 16	10 253	-296 14	15W	20	-53 36	13W	64	-87 42	2 112	64 22	7W	0	-33 23										
9W	0	45 45	28 63	73 21	17 81	77 29	3 668	-717 14	15 81	-124 35	*** 8	8	L	***	22W	26	-43 25	14 406	402 8	17W	34	11 25	*** 13	10	L	***	6 48	-26 50											
11W	49	-27 41	*** 9	6	L	***	5 148	112 32	17W	69	50 51	0 302	323 18	24 140	137 7	18 571	-515 11	19 91	72 10	*** 13	10	L	***	6 182	-177 14	11 61	-61 12												
13W	0	-55 39	*** 9	6	L	***	7 111	54 43	19W	0	-43 44	4 889	-289 16	9 528	-537 14	21W	0	-16 38	8W	0	-6103	26 77	-62 13	*** 15	9	L	***	3 243	-191 12										
15W	21	6 17	1 116	162 40	*** 14	6	L	***	11 358	-309 17	23W	34	-50 24	12 293	-251 12	1 104	59 19	*** 13	8	L	***	2W	0	-21 45	7 106	92 24	12W	0	13 40										
*** 17	1	L	***	2 138	-100 15	7W	0	96105	4 445	412 11	13 249	278 14	16 315	327 12	3W	0	-116 64	5 88	92 35	1 129	157 26	6 227	194 11	11 130	-163 19	16W	45	-10 24											
4W	0	76 42	9W	0	-64 06	6 184	189 16	15 179	170 18	*** 13	7	L	***	20 386	-373 10	5 79	92 35	3 286	-261 13	8W	36	-47 36	13W	64	-87 42	18 81	85 17												
6W	0	50 41	11 104	-70 27	8 610	-580 17	17 136	-126 23	2 427	448 11	24 73	5 26	7 79	-31 35	9W	0	27 56	5 255	269 14	10 207	-195 11	15W	28	30 36															
8 69	45 27	13W	0	-76 65	10W	40	79 54	19 195	-203 17	4 170	180 18	28 64	-67 15	9W	0	27 56	5 255	269 14	10 207	-195 11	15W	28	30 36																
10 126	-137 16	15 214	-210 16	12 309	312 11	21 188	219 17	6 557	-576 8	*** 9	8	L	***	11W	0	-10 57	7 122	-111 24	12W	12	-27 34	17W	0	14 27															
16W	0	2 19	17 101	57 30	14 134	-109 18	23M	62	54 49	8 85	-65 36	*** 9	8	L	***	13W	0	-41 52	9 67	67 63	14W	50	48 26 19	67	-23 15	11W	0	14 27											
*** 18	5	L	***	19 150	-137 21	16 208	-207 17	25W	0	17 41	10 555	512 11	1 478	-421 14	15W	0	-6 46	11 93	-64 33	16 49	25 21	*** 14	10	L	***	*** 14	10	L	***	3 116	86 10								
1 105	89 17	23 81	-33 29	22W	34	-1 19	29W	0	3 18	14 395	-382 10	5 360	342 16	21W	0	-11 23	15 138	81 22	17W	0	-37 57	3 99	-48 18	4 148	148 17	11W	0	15 29											
3W	42	82 35	25W	0	12 41	*** 15	6	L	***	16 135	118 17	7 273	-271 12	9 127	-142 25	19 148	-118 16	21 77	35 27	5W	0	-76 39	6W	15	-139 45	10 133	142 10												
5 62	-23 26	*** 10	6	L	***	1W	25	-35 57	2 278	289 20	11 232	216 15	13 114	147 29	4W	0	-26 25	5 255	269 14	10 207	-195 11	15W	28	30 36															
9 86	72 15	0 121	67 41	3 85	50 31	4 237	-208 22	*** 14	7	L	***	*** 14	7	L	***	6 127	-98 21	8 212	207 14	10 75	-50 32	2 582	-559 11	4W	0	-77 62													
11 59	76 19	2 104	-67 41	5W	0	-28 64	6W	78	78 02	*** 14	7	L	***	10 75	-50 32	2 582	-559 11	4W	0	-77 62	6 521	511 11	2 136	-127 11	*** 15	10	L	***	8 53	47 25									
13W	41	-16 18	4 102	-27 47	7 112	-26 21	8 164	121 31	3 93	119	330 31 11	21 87	138 30	23W	0	-16 40	12 280	-257 10	4W	0	-77 62	6 521	511 11	2 136	-127 11	*** 15	10	L	***	10 133	142 10								
*** 19	5	L	***	6 123	-123 42	9 88	30 27	10 99	-93 30	5W	0	-23 59	7 84	112 34	23W	0	-16 40	12 280	-257 10	4W	0	-77 62	6 521	511 11	2 136	-127 11	*** 15	10	L	***	12W	32	25 20						
2 60	-19 20	8 195	-169 27	11W	0	-18 48	12 80	5 39	5W	0	-23 59	7 84	112 34	23W	0	-16 40	12 280	-257 10	4W	0	-77 62	6 521	511 11	2 136	-127 11	*** 15	10	L	***	14W	44	30 41							
4 47	-13 23	10 166	145 19	13W	49	-7 42	14 80	-23 39	9W	34	-5 54	22 29	27W	25	-23 19	16 88	-46 20	8W	58	-19 59	4W	36	25 2																

chlorate ion do not describe a regular tetrahedral ion, the refinement was terminated. We could see no further hope of improving the model for the disordered perchlorate ion. Our Fourier and difference maps suggest that the twofold disorder allowed for in our structure-factor calculations is only a good first approximation to the true situation. The disorder can be of a much more general nature so long as the twofold symmetry is maintained. For example, there may be disorder

about the axis O(1)–Cl superposed on the disorder about the twofold axis.

The observed structure-factor magnitudes $|F_o|$ and the calculated structure factors F_c are listed in Table 2. Each entry $|F_o|$ has been scaled by the factor $1/S$, where S is the appropriate scale factor on F_c established in the least-squares refinement. For each reflection for which $|F_o|^2$ is equal to or greater than $\sigma(F^2)$, the standard error $\sigma(F)$, computed as $\sigma(F^2)/2|F_o|$, is

Table 3. Parameters of the structure of $\text{Ni}(3,5\text{-dimethylpyridine})_4(\text{ClO}_4)_2$

The elements β_{ij} form the matrix β in the anisotropic temperature factor $\exp(-\mathbf{h}^T \beta \mathbf{h})$, where \mathbf{h} is the vector of reflection indices. The parameter B given for each hydrogen atom is the parameter of the isotropic temperature factor $\exp(-B \sin^2 \theta/\lambda^2)$. The least-squares standard errors are indicated in parentheses. Each hydrogen atom is given the same identifying number as the carbon atom to which it is attached and when necessary an alphabetic identifier.

	Fractional coordinates $\times 10^5$			Elements $\beta_{ij} \times 10^5$					
	<i>x</i>	<i>y</i>	<i>z</i>	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Ni	0 *	$\frac{1}{2}$ *	$\frac{1}{8}$ *	509 (4)	509 †	121 (2)	102 (5)	0 *	0 *
N	6891 (17)	18684 (18)	18015 (8)	469 (14)	630 (17)	128 (3)	125 (11)	-19 (6)	20 (6)
C(1)	15268 (22)	18167 (25)	17657 (12)	468 (17)	628 (20)	148 (5)	110 (15)	-10 (8)	-13 (8)
C(2)	20402 (24)	14720 (24)	21210 (13)	528 (19)	614 (20)	183 (6)	154 (15)	-55 (8)	-66 (9)
C(3)	16473 (27)	11558 (27)	25425 (15)	685 (22)	772 (25)	179 (6)	167 (20)	-115 (10)	-7 (10)
C(4)	7922 (25)	11890 (25)	25942 (12)	686 (22)	763 (23)	151 (5)	128 (18)	-26 (9)	53 (9)
C(5)	3257 (26)	15413 (28)	22125 (13)	484 (17)	745 (22)	149 (5)	72 (16)	-4 (7)	62 (9)
C(6)	29766 (35)	14458 (55)	20556 (28)	549 (25)	1008 (41)	325 (11)	184 (26)	-87 (14)	-89 (19)
C(7)	3321 (56)	8374 (71)	30505 (23)	1000 (44)	1542 (62)	203 (8)	217 (49)	68 (17)	226 (20)
Cl	-16249 (63)	10248 (65)	12733 (95)	613 (33)	547 (22)	197 (10)	-91 (26)	57 (22)	-85 (14)
O(1)	15507 (59)	-9734 (57)	13803 (15)	620 (33)	640 (34)	185 (11)	-127 (18)	78 (20)	-108 (21)
O(2)	-23808 (68)	13868 (80)	13452 (37)	488 (37)	1953 (86)	381 (24)	-18 (45)	99 (23)	-359 (34)
O(3)	9408 (53)	-15906 (62)	6913 (22)	1505 (67)	1314 (59)	201 (10)	-470 (50)	34 (23)	-221 (22)
O(4)	2967 (82)	-15925 (127)	14366 (68)	3194 (212)	821 (83)	701 (48)	635 (109)	-394 (69)	439 (49)

	Fractional coordinates $\times 10^4$			<i>B</i> (Å ²)	Fractional coordinates $\times 10^4$			<i>B</i> (Å ²)	
	<i>x</i>	<i>y</i>	<i>z</i>		<i>x</i>	<i>y</i>	<i>z</i>		
H(1)	1726 (22)	2100 (21)	1479 (12)	7.3 (1.1)	H(6c)	3123 (39)	1050 (40)	1895 (22)	15.4 (3.0)
H(3)	1995 (24)	1000 (23)	2785 (13)	7.7 (1.2)	H(7a)	44 (31)	1268 (23)	3237 (14)	8.5 (1.5)
H(5)	-269 (19)	1543 (19)	2235 (99)	4.4 (0.8)	H(7b)	-79 (46)	443 (44)	2993 (21)	17.8 (4.0)
H(6a)	3237 (42)	1969 (44)	1952 (23)	19.2 (3.4)	H(7c)	734 (44)	956 (44)	3278 (25)	17.8 (3.1)
H(6b)	3286 (36)	1361 (34)	2365 (21)	14.4 (2.3)					

* Parameter fixed by symmetry.

† β_{22} of Ni is constrained equal to β_{11} by symmetry.

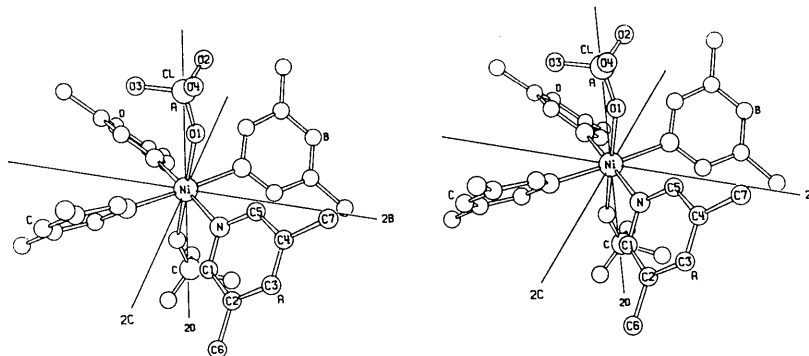


Fig. 1. Stereoscopic drawing of the octahedral complex $\text{Ni}(3,5\text{-dimethylpyridine})_4(\text{ClO}_4)_2$. The axes labelled 2B, 2C, and 2D are the three twofold axes of the point group 222. See text for explanation of other labelling in the Figure. Each disordered perchlorate ion is shown in only one of its two orientations about the axis 2D. Hydrogen atoms are not shown.

given; for the other reflections, marked *W* in the table, $\sigma(F^2)$ is given. The reflections marked *X* were in the group of reflections thought to be subject to extinction error and omitted in the final refinement. The final atomic parameters and their standard errors appear in Table 3.

Discussion

A main feature of interest in our results is the confirmation that the nickel atom is coordinated to two perchlorate ligands as well as to the four organic ligands. The structure of the octahedral complex is represented in the stereoscopic drawing of Fig. 1 and is described in some detail by the bond-length and angle data of Table 4 and the non-bonded distances of Table 5. In Fig. 1 the atoms of the dimethylpyridine group and the half-weight perchlorate group of the asymmetric unit are labelled individually, and the two groups are labelled *A*. The groups labelled *B*, *C*, and *D* are related to *A* by rotations about the twofold axes *2B*, *2C*, and *2D* shown in the Figure. These are the axes $0, \frac{1}{4}, z, x, \frac{1}{4} - x, \frac{1}{8}$, and $x, \frac{1}{4} + x, \frac{1}{8}$. In Tables 4 and 5 the letters *A*, *B*, *C*, and *D* are included in the atom designations when necessary to distinguish atoms related by symmetry. An atom designation without a letter is equivalent to one with the letter *A*.

We emphasize that the problem of disorder of the arrangement of the perchlorate ions has not led to any

Table 5. *Some intramolecular non-bonded distances in Ni(3,5-dimethylpyridine)₄(ClO₄)₂*

N(A)–N(C)	2·954 (4) Å	C(1A)–C(1C)	3·347 (7) Å
N(A)–N(B)	2·968 (5)	C(1A)–O(1B)	2·925 (11)
N(A)–C(1C)	3·190 (4)	C(1A)–O(1C)	3·278 (10)
N(A)–C(5B)	3·191 (5)	C(1A)–O(2B)	3·352 (12)
N(A)–O(1A)	2·914 (8)	C(5A)–C(5B)	3·215 (9)
N(A)–O(1B)	2·788 (7)	C(5A)–O(1A)	3·035 (9)
N(A)–O(1C)	3·161 (6)	C(5A)–O(1D)	3·557 (8)
N(A)–O(1D)	3·223 (8)	C(5A)–O(3D)	3·336 (9)

ambiguity in regard to the coordination of perchlorate. Although the perchlorate ion described by our parameters is somewhat distorted (see the bond lengths and angles in Table 4), it is still a fair approximation to the tetrahedral ion expected. Furthermore, the oxygen atom of most interest, O(1), is positioned more precisely than any other atom of the perchlorate group except O(3) and about as precisely as atoms C(6) and C(7). The root-mean-square principal-axis vibrational amplitudes of O(1) are comparable to those of the atoms of the organic ligands and are quite reasonable (Table 6).

The atom O(1) is at a distance of 0·350(4) Å from the nearby twofold axis (axis *2D* in Fig. 1). Therefore, the complex – even that part of it consisting of the nickel atom and the atoms immediately attached to it – does not, except in the statistical sense, have the expected symmetry consistent with the location of the

Table 4. *Bond lengths and angles in the complex molecule Ni(3,5-dimethylpyridine)₄(ClO₄)₂*

Each angle specified by four atoms, as *a*–*b*–*c*–*d*, is a torsion angle, defined to be the angle measured clockwise from the projection of *ba* to the projection of *cd* viewed in the direction of *bc*. The indicated standard errors were calculated from the least-squares covariance matrix. For the key to the numbering of the atoms see Fig. 1 and the text.

Ni—O(1)	2·187 (4) Å	Ni—N—C(2)	120·0 (2)°
Ni—N	2·093 (2)	Ni—N—C(5)	122·5 (2)
N(A)–Ni—N(B)	90·3 (1)°	C(1)–N—C(5)	117·5 (2)
N(A)–Ni—N(C)	89·8 (1)	N—C(1)–C(2)	124·7 (3)
N(A)–Ni—N(D)	176·5 (2)	C(1)–C(2)–C(3)	116·3 (4)
N(A)–Ni—O(1A)	87·8 (3)	C(1)–C(2)–C(6)	121·5 (5)
N(A)–Ni—O(1B)	81·3 (2)	C(3)–C(2)–C(6)	122·2 (4)
N(A)–Ni—O(1C)	95·2 (2)	C(2)–C(3)–C(4)	121·1 (4)
N(A)–Ni—O(1D)	97·7 (3)	C(3)–C(4)–C(5)	118·3 (4)
Cl—O(1)	1·40 (1) Å	C(3)–C(4)–C(7)	122·8 (4)
Cl—O(2)	1·34 (2)	C(5)–C(4)–C(7)	118·9 (5)
Cl—O(3)	1·45 (3)	C(4)–C(5)–N	122·1 (4)
Cl—O(4)	1·24 (2)	N—C(1)–C(2)–C(3)	0·3 (6)
O(1)–Cl—O(2)	113 (1)°	N—C(1)–C(2)–C(6)	–179·3 (5)
O(1)–Cl—O(3)	104 (1)	C(1)–C(2)–C(3)–C(4)	0·2 (6)
O(1)–Cl—O(4)	119 (2)	C(6)–C(2)–C(3)–C(4)	179·8 (5)
O(2)–Cl—O(3)	102 (1)	C(2)–C(3)–C(4)–C(5)	0·5 (6)
O(2)–Cl—O(4)	113 (1)	C(2)–C(3)–C(4)–C(7)	179·2 (6)
O(3)–Cl—O(4)	106 (1)	C(3)–C(4)–C(5)–N	1·7 (6)
N—C(1)	1·336 (4) Å	C(7)–C(4)–C(5)–N	179·5 (6)
N—C(5)	1·346 (4)	C(4)–C(5)–N—C(1)	2·2 (6)
C(1)–C(2)	1·367 (4)	C(4)–C(5)–N—N	–174·4 (3)
C(2)–C(3)	1·383 (5)	C(5)–N—C(1)–C(2)	–1·5 (6)
C(3)–C(4)	1·366 (5)	Ni—N—C(1)–C(2)	175·2 (3)
C(4)–C(5)	1·380 (4)		
C(2)–C(6)	1·497 (6)		
C(4)–C(7)	1·528 (7)		

Table 6. Atomic root-mean-square displacements in the directions of the principal axes of the thermal ellipsoids

	R.m.s.d. (Å) in direction of axis		
	1	2	3
Ni	0.210 (2)	0.228 (2)	0.279 (2)
N	0.207 (3)	0.234 (3)	0.299 (4)
C(1)	0.229 (4)	0.231 (4)	0.296 (5)
C(2)	0.229 (5)	0.239 (4)	0.321 (5)
C(3)	0.216 (5)	0.289 (5)	0.347 (6)
C(4)	0.222 (4)	0.283 (5)	0.332 (5)
C(5)	0.221 (4)	0.247 (4)	0.318 (5)
C(6)	0.238 (6)	0.344 (7)	0.473 (10)
C(7)	0.244 (6)	0.322 (7)	0.392 (8)
Cl	0.229 (10)	0.257 (6)	0.318 (9)
O(1)	0.221 (11)	0.255 (5)	0.338 (9)
O(2)	0.233 (10)	0.325 (11)	0.538 (12)
O(3)	0.225 (7)	0.365 (9)	0.499 (10)
O(4)	0.234 (12)	0.482 (15)	0.693 (21)

nickel atom. The chlorine atom is 0.179(12) Å from axis 2*D*; and the angle Ni–O(1)–Cl is 158.0(1.1)°. The twofold disorder of the perchlorate arrangement is quite similar to the fourfold disorder of the one perchlorate ion coordinated to cobalt in Co(diphenylmethylarsine oxide)₄(ClO₄)₂ (Pauling *et al.*, 1965). In the latter compound the oxygen corresponding to our O(1) is 0.72 Å from the fourfold axis, the chlorine atom is either on or very near the axis, and the Co–O–Cl angle is 130°. The disorder in our compound is also similar to that reported from the structure analysis of [Ni(ethylenediamine)₂NO₂]BF₄ (Drew, Goodgame, Hitchman & Rogers, 1965), in which a half-oxygen atom and a half-nitrogen atom correspond to our two half-oxygen sites (1*A*) and (1*D*) (though the point-group symmetry of the disordered complex molecule is $\bar{1}$ and the symmetry element involved in the disorder is a mirror). In this case the N–Ni–O angle* is 24.2°, to be compared with our O(1*A*)–Ni–O(1*D*) angle* of 18.5(2)°.

Our Ni–O(1) distance of 2.187(4) Å is not significantly different from the Ni–O distance 2.215(17) Å reported in [Ni(ethylenediamine)₂NO₂]BF₄. Somewhat smaller distances have been reported in other octahedral complexes of nickel; for example, 2.085(12), 2.083(12), and 2.036(12) Å in nickel ammonium sulfate hexahydrate (Montgomery & Lingafelter, 1964) and 2.107(8) Å in dinitritobis-(*N,N*-dimethylethylenediamine)nickel(II) (Drew, Goodgame, Hitchman & Rogers, 1964).

The distance Ni–N of 2.093(2) Å found in the present work is in the middle range of values reported in other octahedral complexes of nickel: 2.00(5) Å in bischlorotetrakispyridine-nickel(II) (Porai-Koshits, 1954; *Structure Reports*, 1954, p. 749); 2.120(13) Å in tris(ethylenediamine)nickel(II) nitrate (Swink & Atoji, 1960); 2.089(9) and 2.219(12) Å in dinitritobis-(*N,N*-dimethylethylenediamine)nickel(II) (Drew *et al.*, 1964);

2.097(12), 2.117(11), and 2.155(19) Å in [Ni(ethylenediamine)₂NO₂]BF₄ (Drew *et al.*, 1965).

The C–N bond lengths in the dimethylpyridine ligand average 1.341 Å, very close to the value 1.3402(10) Å reported from a microwave study (Bak, Hansen-Nygaard & Rastrup-Andersen, 1958) of pyridine. The ring C–C bond lengths average 1.370 Å, somewhat lower than the average value of 1.3945(10) Å reported from the microwave study. The two external C–C bond lengths average 1.513 Å, close to the average value of 1.505(5) Å for a number of bonds between tetrahedral carbon atoms and aromatic rings (*Tables of Interatomic Distances*, 1965, page S15s). The atoms of the organic ligand are not quite coplanar, as indicated by the deviations of the torsion angles about the ring bonds from the values 0° and 180° characteristic of a plane structure (see Table 4). The apparent departure from the symmetry *mm2* expected for an isolated molecule of 3,5-dimethylpyridine probably is not of much significance and is partly the result of 'noise' resulting from the incomplete model for the perchlorate disorder.

The 3,5-dimethylpyridine ligands form the blades of a four-bladed propeller. The angle between the average plane of each of the four organic groups and the plane perpendicular to the twofold axis through the perchlorate ions is 46.6°. The configuration of the nickel atom and the four nitrogen atoms in each molecule is not quite plane; the nitrogen atoms are alternately 0.065 Å above and 0.065 Å below their average plane through the nickel atom. The torsion angles C(4)–C(5)–N–Ni and Ni–N–C(1)–C(2), –174.4(3)° and 175.2(3)° respectively, and the angle Ni–N–C(3) of 175.6(2)° show that the N–Ni bond is bent significantly out of the average plane of the organic ligand.

The geometry of the complex molecule and the packing of the molecules in the crystal (see the stereoscopic drawing of Fig. 2) are very similar to the geometry and packing reported for Ni(pyridine)₄Cl₂ (Porai-Koshits, 1954; *Structure Reports*, 1954, p. 749). Crystals of this compound also have the space-group symmetry *I*₄/*acd*, with cell translations *a* and *b* identical within experimental error with those of our compound and with a translation *c* of 16.90(5) Å. The nickel and chlorine atoms are in the same kinds of special positions as the nickel atom and the centroid of the disordered perchlorate in our structure.

As is usually the case in X-ray structure analysis, the apparent C–H bond lengths are short, varying from 0.80 Å to 0.97 Å. Otherwise the approximate positions established for the hydrogen atoms make good chemical sense, except that one of the hydrogen atoms of the methyl carbon C(7) is rather grossly misplaced, by 25° to 30°, in its orientation about the axis C(4)–C(7).

The contacts between the adjacent organic ligands within the complex molecule are of the types N(1*A*)...C(1*C*)H, N(1*A*)...C(5*B*)H, C(1*A*)H...C(1*C*)H, and C(5*A*)H...C(5*B*)H. The distances corresponding to these and other non-bonded contacts within the molecule seem reasonable (see Table 5). The N(1*A*)...

* These angles are, of course, not valence angles but angles defined by the nickel atoms and possible sites for the atoms in disorder.

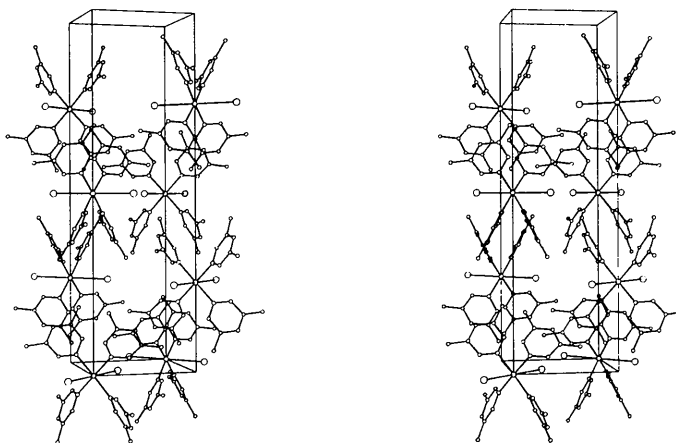


Fig. 2. Packing of the complex molecules $\text{Ni}(\text{3,5-dimethylpyridine})_4(\text{ClO}_4)_2$ in the crystal structure. The origin of the axial system in this Figure is at the lower left rear corner, a site of point-group symmetry $\bar{4}$ which has coordinates $0, \frac{1}{4}, \frac{1}{4}$ with reference to the origin at $\bar{1}$ to which our atomic coordinates are referred. A screw axis 4_1 parallel to c runs through the center of the parallelepiped, which has dimensions $a/2, b/2, c$. Each disordered perchlorate group is represented by a circle corresponding to its centroid.

$\text{C}(5B)$ and $\text{C}(5A) \cdots \text{C}(5B)$ distances of about 3.2 \AA are slightly less than the aromatic ring thickness ($\sim 3.40 \text{ \AA}$) but are consistent with the relative orientation of the two ligands A and B (see Fig. 1). The closest intermolecular contacts of various kinds are as follows: $\text{CH}_3 \cdots \text{O}$, $3.241(10), 3.296(14), 3.480(16) \text{ \AA}$; $\text{CH} \cdots \text{O}$, $3.358(9), 3.372(11) \text{ \AA}$; $\text{CH} \cdots \text{CH}$, $3.677(9) \text{ \AA}$; $\text{CH}_3 \cdots \text{CH}_3$, $3.873(10), 3.969(21), 4.226(10) \text{ \AA}$. Of these the first two distances are slightly but not impossibly short.

Computations for this work were carried out on CDC 1604, IBM 7090, and IBM 360/75 computers. Programs used, with accession numbers in the *World List of Crystallographic Computer Programs* (Shoemaker, 1966), are as follows:

Absorption correction	ORABS ¹	–
Statistical analysis of data	ORSTAT	496
Fourier synthesis	XFOUR ²	391
Least-squares refinement	XFLS ³	389
Distances and angles	ORFFE ³	363
Structure drawings	ORTEP	387
Structure-factor table	EDIT ⁴	393

[(1) Wehe, Busing & Levy, 1962, revised for the CDC 1604 by R.D.Ellison & H.A.Levy. (2) Modified for the IBM 360/75 by G.Brunton. (3) Modified for the IBM 360/75 by C.K.Johnson. (4) New version with variable format for output.]

We thank Professor W.E.Bull for suggesting this work and for providing the subject material. One of us (F.M.-A.) gratefully acknowledges the hospitality of the Oak Ridge National Laboratory.

References

- BAK, B., HANSEN-NYGAARD, L. & RASTRUP-ANDERSEN, J. (1958). *J. Mol. Spect.* **2**, 361.
- BUFFAGNI, S., VALLARINO, L. M. & QUAGLIANO, J. V. (1964). *Inorg. Chem.* **3**, 671.
- BUSING, W. R., ELLISON, R. D., LEVY, H. A., KING, S. P. & ROSEBERRY, R. T. (1968). *The Oak Ridge Computer-Controlled X-ray Diffractometer*. Report ORNL-4143, Oak Ridge National Laboratory, Tennessee.
- BUSING, W. R. & LEVY, H. A. (1967). *Acta Cryst.* **10**, 180.
- COTTON, F. A. & WEAVER, D. L. (1965). *J. Amer. Chem. Soc.* **87**, 4189.
- DONOHUE, J. & TRUEBLOOD, K. N. (1952). *Acta Cryst.* **5**, 414.
- DREW, M. G. B., GOODGAME, D. M. L., HITCHMAN, M. A. & ROGERS, D. (1964). *Proc. Chem. Soc.* p. 363.
- DREW, M. G. B., GOODGAME, D. M. L., HITCHMAN, M. A. & ROGERS, D. (1965). *Chem. Comm.* p. 477.
- International Tables for X-ray Crystallography* (1952). Vol. I. Birmingham: Kynoch Press.
- International Tables for X-ray Crystallography* (1962). Vol. III. Birmingham: Kynoch Press.
- MADAULE-AUBRY, F., BUSING, W. R. & BROWN, G. M. (1968). *Acta Cryst.* **B24**, 754.
- MONTGOMERY, H. & LINGAFELTER, E. C. (1964). *Acta Cryst.* **17**, 1478.
- MOORE, L. E., GAYHART, R. B. & BULL, W. E. (1964). *J. Inorg. Nuclear Chem.* **26**, 896.
- PAULING, P., ROBERTSON, G. B. & RODLEY, G. A. (1965). *Nature, Lond.* **207**, 74.
- PORAI-KOSHITS, M. A. (1954). *Trudy Inst. Krist. Akad. Nauk SSSR*, p. 117.
- ROSENTHAL, M. R. & DRAGO, R. S. (1965). *Inorg. Chem.* **4**, 840.
- SHOEMAKER, D. P. (1966). *World List of Crystallographic Computer Programs*, 2nd Edition. Utrecht: Oosthoek.
- STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175.
- Structure Reports* (1954). Vol. 18. Utrecht: Oosthoek, 1961.
- SWINK, L. N. & ATOJI, M. (1960). *Acta Cryst.* **13**, 639.
- Tables of Interatomic Distances and Configuration in Molecules and Ions* (1965). Special Publication No. 18. London: The Chemical Society.
- WEHE, D. J., BUSING, W. R. & LEVY, H. A. (1962). *A Fortran Program for Calculating Single Crystal Absorption Corrections*. Technical Memorandum 229. Oak Ridge National Laboratory, Tennessee.
- WILSON, A. J. C. (1942). *Nature, Lond.* **150**, 151.
- WOOLFSON, M. M. (1956). *Acta Cryst.* **9**, 804.