756. *The Magnetic Susceptibility and Crystal Structure of Nitritobis(ethylenediamine)nickel Perchlorate.*

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A two-dimensional *X*-ray analysis of the paramagnetic compound $[NiNO_2\ en_2]ClO_4$ ($\mu = 3{\cdot}23$ B.M.) has shown the octahedral configuration for nickel. A chain structure is found in which two nickel atoms are linked by the same oxygen atom of a nitrite group present in the nitrito-form. The nickel–oxygen bond distance is 2·58 Å.

It was reported [1] that a stable compound nitritobis(ethylenediamine)nickel perchlorate, $[NiNO_2\ en_2]ClO_4$, crystallizes from a solution of bisethylenediaminenickel diperchlorate containing sodium nitrite. The complex was paramagnetic but no accurate susceptibility measurements had been made. This paper describes such measurements and a single-crystal, two-dimensional, *X*-ray analysis.

Experimental

Magnetic Susceptibility.—Red needles of the salt $[NiNO_2\ en_2]ClO_4$ were prepared (Found: C, 14·7; H, 4·7; Ni, 18·2; N, 21·0; NO_2, 14·2. $C_4H_{16}ClNiN_5O_6$ requires C, 14·8; H, 5·0; Ni, 18·1; N, 21·6; NO_2, 14·2%) as described by Curtis.[1] Magnetic-susceptibility measurements from 90° to 298° K were made on the solid compound by the Gouy method. The results are shown in Table 1, corrections for diamagnetism being made.[2,3] The compound obeyed the Curie–Weiss law over the temperature range investigated ($\Delta = 107°$) and a magnetic moment of 3·23 B.M./molecule was calculated.

Table 1.

Temp. (°K)	298°	195°	90°
$10^6\chi_M'$	3186	4338	6521

χ_M' = molar susceptibility including the diamagnetic correction.

X-Ray Analysis.—The crystals were needles elongated along [*b*] and showing well-developed (001) and (011) faces. The crystal data were: $C_4H_{16}ClN_5NiO_6$. $M = 324{\cdot}4$. Orthorhombic $a = 15{\cdot}16 \pm 0{\cdot}06$, $b = 10{\cdot}24 \pm 0{\cdot}04$, $c = 8{\cdot}28 \pm 0{\cdot}03$ Å. $U = 1285$ Å^3. $D_m = 1{\cdot}66$ (by flotation). $Z = 4$. $D_c = 1{\cdot}676$. $F(000) = 672$. Space group, $Pnma$ (D_{2h}^{16}, No. 62) or $Pn2_1a$ (C_{2v}^9, No. 33). Cu-K_α radiation; single-crystal rotation and Weissenberg photographs. The statistical test of Howells, Phillips, and Rogers [4] favoured a centrosymmetric (001) projection. Insufficient reflexions for the test (only 42) were recorded for the (100) projection. The (010) projection is centrosymmetric for both space groups. Intensity data were recorded for the *h*0*l*, 0*kl*, and *hk*0 zones by the multiple-film technique. Relative intensities were measured by visual comparison with a standard scale and converted into structure amplitudes. No absorption corrections were applied since small crystals were used.

The Patterson projections $P(u,w)$ and $P(u,v)$ were consistent with the following atomic co-ordinates for nickel and chlorine atoms: Ni, $x = y = z = 0{\cdot}00$; Cl, $x = 0{\cdot}16$, $y = 0{\cdot}25$, $z = 0{\cdot}43$. These atoms correspond to special positions (*a*) and (*c*) of space group $Pnma$ or to the general positions of $Pn2_1a$. For space group $Pn2_1a$ the (010) projection was studied by assuming these nickel and chlorine positions and allotting their signs to the majority of the *h*0*l* amplitudes. In the resulting Fourier synthesis atoms of one ethylenediamine group and oxygens of the perchlorate group were located. After adjustment of co-ordinates by a series of partial difference syntheses, atomic co-ordinates of the second ethylenediamine group were found. They lay directly above the atoms of the first ethylenediamine group and deviations from these positions were not detected. On refinement by further partial-difference syntheses

[1] Curtis, Thesis, University of New Zealand, 1954.
[2] Jagannadham, *Proc. Rajasthan Acad. Sci.*, 1950, **1**, 6; *Chem. Abs.*, 1951, **45**, 9948.
[3] Selwood, "Magnetochemistry," Interscience Publ., Inc., New York, 1943.
[4] Howells, Phillips, and Rogers, *Acta Cryst.*, 1950, **3**, 210.

the remaining three light atoms (the NO_2 group) were located. The scale factor and isotropic-temperature factors for nickel and chlorine were established by least-squares adjustment. An overall temperature factor was assigned to the light atoms, except O_6, which required a

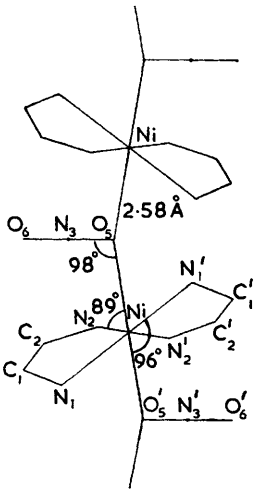

FIG. 1. Diagram of the structure viewed along the *c*-axis.

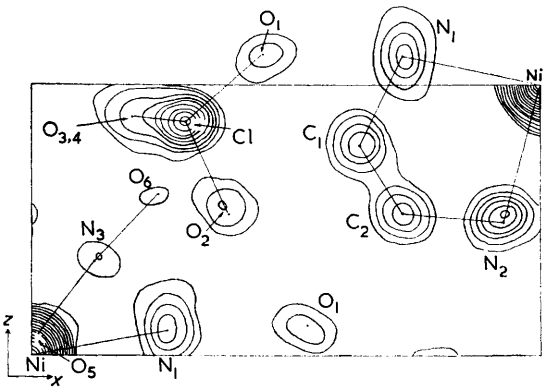

FIG. 2. Electron density along the *b*-axis. Contours are at intervals of 3 eÅ^{-2} (6 eÅ^{-2} at nickel). Lowest contour at 6 eÅ^{-2}.

substantially higher value. Structure factors were calculated with the atomic scattering factors of Berghuis *et al.*[5] for the light atoms and chlorine, and Thomas–Fermi [6] values for nickel. The final *R*-value was 17·3% (all planes).

TABLE 2.

	x	*y*	*z*		*x*	*y*	*z*		*x*	*y*	*z*
Ni	0·500	0·000	0·500	O_4	0·101	0·385	0·444	N_2	0·466	0·026	0·253
Cl	0·153	0·250	0·430	O_5	0·011	0·750	0·038	N_3	0·062	0·750	0·172
O_1	0·229	0·250	0·556	O_6	0·123	0·750	0·296	C_1	0·324	−0·059	0·387
O_2	0·194	0·250	0·260	N_1	0·362	−0·040	0·549	C_2	0·364	0·036	0·265
O_3	0·101	0·115	0·444								

TABLE 3.

		Ni	Cl	Light atoms	O_6
Projection (010)	B	2·0	2·5	3·0	6·0
Projection (001)	B	1·4	1·7	3·0	6·0

TABLE 4.

Bond lengths (Å) and angles.

Ni–N_1	2·17	N_3–O_5	1·35	N_1–Ni–N_2	88°	Ni–O_5–N_3	98°
Ni–N_2	2·13	N_3–O_6	1·38	Ni–N_1–C_1	103	O_5–N_3–O_6	173
C_1–C_2	1·53	Cl–O_1	1·55	N_1–C_1–C_2	111	O_1–Cl–O_2	108
N_1–C_1	1·47	Cl–O_2	1·54	C_1–C_2–N_2	113	O_2–Cl–O_3	105
N_2–C_2	1·55	Cl–O_3	1·60	Ni–N_2–C_2	101	O_3–Cl–O_4	120
Ni–O_5	2·58	Cl–O_4	1·60	O_5–Ni–N_1	96	O_1–Cl–O_4	109
				O_5–Ni–N_2	89		

The space group $Pn2_1a$ was also applied to the (001) projection. The nickel and the chlorine position obtained from $P(u,v)$ were used to determine the phase angles of the majority of the *hk*0 planes. Models of the ethylenediamine and the perchlorate group were superimposed on

[5] Berghuis, Haanappel, Potters, Loopstra, MacGillavry, and Veenendaal, *Acta Cryst.*, 1955, **8**, 478.
[6] Thomas and Fermi; as compiled in " Internationale Tabellen," 1935, Vol. II, p. 572.

the Fourier synthesis by using the known x-co-ordinates as a guide. Atomic positions were obtained, care being taken to avoid introducing a mirror plane. On subsequent refinement by partial-difference syntheses the NO_2 group was located and at the same time mirror planes appeared at $y = \frac{1}{4}, \frac{3}{4}$. This and the superposition of the ethylenediamine groups in the (010) projection indicate that any departure from space group *Pnma* must be slight. The final R-value was 21·8%.

TABLE 5.

	$\sigma(d)$ (Å)		$\sigma(\theta)$		$\sigma(\theta)$
Light–Light atoms	0·052	3 Light atoms	3·5°	Light atom–Ni–Light atom	1·3°
Cl–Light atoms ...	0·040	Ni–Light–Light atoms	2·3	Light atom–Cl–Light atom	2·1
Ni–Light atoms ...	0·037				

TABLE 6.

Observed structure amplitudes and calculated structure factors (× 10).

h k l	$\lvert F_o\rvert$	F_c	h k l	$\lvert F_o\rvert$	F_c	h k l	$\lvert F_o\rvert$	F_c	h k l	$\lvert F_o\rvert$	F_c	h k l	$\lvert F_o\rvert$	F_c
*h*0*l* zone			0 0 4	1143	1234	2	269	338	18	<62	134	3	200	−162
0 0 0	—	6720	1	<87	42	3	<124	−57				5	578	−470
2	826	963	2	948	854	4	290	475	2 5 0	322	−261	7	<189	145
4	<81	−296	3	335	342	5	<118	119	4	885	961	9	167	55
6	1482	1301	4	705	595	6	199	309	6	<112	64			
8	904	898	5	285	−86	7	161	−82	8	254	−191	0 2 0	773	558
10	205	245	6	501	523	8	155	107	10	274	236	2	217	316
12	393	355	7	<101	102	9	178	−103	12	441	277	4	756	708
14	441	400	8	669	659	10	189	272	14	<130	−138	6	478	374
16	232	168	9	226	−239				16	<105	−20	8	629	603
18	134	159	10	356	386	1 0 9	216	328				10	145	195
			11	318	−236	2	151	134	0 6 0	538	−395			
1 0 1	1011	993	12	<124	81	3	<107	80	2	880	785	0 3 1	373	−486
2	128	−334	13	<101	178	4	<101	6	4	701	741	3	384	68
3	1094	1345	14	333	301	5	158	220	6	496	257	5	<161	−302
4	145	128	15	<95	68	6	<95	−35	8	632	418	7	<189	−297
5	1004	1188	16	222	216	7	184	238	10	578	481	9	<161	−127
6	273	319	17	167	−167				12	254	193			
7	897	899	18	134	79	*hk*0 zone			14	341	193	0 4 0	1779	2346
8	248	284				2 0 0	1041	968	16	<86	308	2	779	301
9	602	410	1 0 5	792	677	4	186	−291				4	829	859
10	205	166	2	451	−471	6	1606	1502	2 7 0	422	373	6	189	72
11	560	449	3	544	539	8	1097	1016	4	254	−158	8	<178	209
12	<118	34	4	399	311	10	212	212	6	<136	−55	10	<89	71
13	242	198	5	399	370	12	484	418	8	312	63			
14	<124	−12	6	367	352	14	484	448	10	241	96	0 5 1	306	−242
15	420	551	7	581	519	16	216	136	12	<130	−58	3	367	290
16	167	−91	8	312	−31	18	130	186	14	<105	140	5	501	−415
17	302	358	9	318	340				16	<62	11	7	<189	165
18	128	43	10	172	141	2 1 0	916	−876				9	<134	−10
			11	172	196	4	985	1053	0 8 0	929	1028			
0 0 2	1055	1097	12	<97	−89	6	322	188	2	404	477	0 6 0	439	−401
1	571	627	13	285	410	8	<105	41	4	304	333	2	540	158
2	592	572	14	189	−109	10	<124	130	6	484	411	4	667	468
3	107	283	15	199	223	12	192	153	8	379	464	6	484	475
4	511	474	16	44	−70	14	241	−202	10	<130	272	8	378	419
5	699	−663				16	<124	21	12	254	316			
6	755	650	0 0 6	222	−243	18	<92	183	14	245	316	0 7 1	<167	−185
7	242	132	1	<112	28							3	484	355
8	926	889	2	513	561	0 2 0	799	558	2 9 0	390	−166	5	<134	−30
9	140	−92	3	195	217	2	991	1222	4	397	326	7	<167	−56
10	544	520	4	560	625	4	335	505	6	<143	152	9	<73	−124
11	318	−82	5	236	−93	6	862	786	8	<136	−22			
12	602	731	6	205	134	8	855	626	10	<124	76	0 8 0	829	960
13	172	200	7	<124	−113	10	428	458	12	<100	167	2	578	528
14	457	408	8	323	279	12	<136	245	14	<56	−88	4	462	464
15	<118	26	9	<124	−35	14	<143	182				6	212	111
16	228	118	10	367	430	16	404	350	0 10 0	245	−180	8	<106	10
17	178	−121	11	167	6	18	<86	141	2	614	474			
18	194	286	12	296	283				4	558	475	0 9 1	189	−246
			13	<107	14	2 3 0	390	−287	6	341	19	3	189	3
1 0 3	642	601	14	216	225	4	619	−649	8	373	250	5	300	−273
2	985	−947				6	<100	278	10	297	473	7	<123	129
3	920	852	1 0 7	362	531	8	353	272	12	<68	177			
4	501	−504	2	383	−371	10	<130	64				0 10 0	295	−191
5	776	710	3	<124	125	12	366	−332	0 12 0	212	368	2	451	221
6	614	567	4	242	−129	14	<136	117	2	192	200	4	334	214
7	832	845	5	323	343	16	118	121	4	180	284	6	262	330
8	679	−491	6	<124	85	18	<82	−150	6	154	322			
9	678	613	7	323	300				8	<49	178	0 11 1	<167	−126
10	490	−238	8	268	−178	0 4 0	2009	2376				3	<156	27
11	463	333	9	236	215	2	707	599	*0kl* zone			5	<111	−42
12	269	152	10	161	−53	4	732	702	0 0 2	1090	1097			
13	302	270	11	259	286	6	1353	1278	4	1196	1235	0 12 0	195	284
14	172	−134	12	<95	−12	8	609	622	6	164	−244	2	206	254
15	350	380	13	222	300	10	<130	−41	8	<189	117	4	123	136
16	222	−105				12	441	355	10	<128	−34			
17	216	194	0 0 8	172	116	14	428	589						
18	157	180	1	268	−210	16	<112	193	0 1 1	401	−149			

Atomic co-ordinates from the (010) and (001) projections were used to calculate structure factors (space group *Pnma*) for the (100) projection. An *R*-value of 23·8% was obtained.

As seen from Fig. 1, the structure is novel: a linear NO_2 group with one oxygen atom shared between two nickel atoms. In view of this the (001) projection was again considered. Calculations were repeated for space group $Pn2_1a$, thus removing the mirror plane and any restriction on the shape of the NO_2 group. However, it was not possible to fit the usual non-linear nitro-form of the NO_2 group to the Fourier syntheses. In addition, attempts to " lose " the mirror plane (by changing the y co-ordinates of the ethylenediamine groups and the perchlorate oxygens or by moving the linear NO_2 group) were unsuccessful.

The x-co-ordinates from the two projections (010), (001) agreed within 0·004 (expressed in fractional co-ordinates) except for atom O_6 where the discrepancy was 0·006. Mean x-co-ordinates were taken and the final atomic co-ordinates and temperature factors are listed in Tables 2 and 3. The electron density projected down [*b*] is shown in Fig. 2. The peaks for O_6 are more diffuse than the peaks for the other oxygen atoms, which probably accounts for the discrepancy in its co-ordinates. Standard deviations of bond length and bond angle were calculated by the methods of Cruickshank [7] and of Cruickshank and Robertson,[8] respectively. Bond lengths and angles are listed in Table 4, standard deviations in Table 5, and values of F_o and F_c in Table 6.

Discussion

The arrangement of the atoms in the structure is shown in Fig. 1. The nickel atoms are each co-ordinated to two terminal oxygen atoms of two nitrito-groups, each of these oxygen atoms being shared between two nickel atoms. The configuration about the nickel is thus octahedral, which is consistent with the observed paramagnetism. The ethylenediamine rings co-ordinated to the nickel atom are in the gauche form. The NO_2 group is present as the nitrito-group (ONO) with one oxygen atom co-ordinated but the other free and undergoing a relatively large thermal vibration. Any slight deviation from space group *Pnma* not detected on the Fourier syntheses could alter the nickel–oxygen bond distances slightly, but the general features of the structure must be the same. Such a deviation would mean that the bridging oxygen atom need no longer be equidistant from the two nickel atoms. However, the NO_2 group must still remain approximately linear since there is no evidence to suggest an angle approaching 120° which would be expected for a normal nitrite group. The perchlorate group is regularly tetrahedral within the limits of the accuracy attained. None of the bond lengths is particularly notable (again considering the accuracy of the determination) except for the long nickel–oxygen bond distance of 2·58 Å which indicates weak bonding. The ultraviolet spectrum of an aqueous solution was observed to be that of the diaquobisethylenediamine nickel cation plus that of the nitrite ion. Thus the chain structure appears to break down in solution.

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[7] Cruickshank, *Acta Cryst.*, 1949, **2**, 65.
[8] Cruickshank and Robertson, *Acta Cryst.*, 1953, **6**, 698.