26. *A Supposed Hydrazine Complex of Ruthenium*(III).

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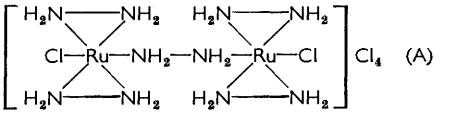
A substance previously formulated as $[Ru_2Cl_2(N_2H_4)_5]Cl_4$ has been proved to be $[RuCl(NH_3)_5]Cl_2$.

The crystal structure has been determined.

During a search for compounds that might contain hydrazine as a ligand, an investigation was made of the substance reported [1] to be formed by the reaction of a hot saturated aqueous solution of hydrazinium(1+) chloride with Howe's salt, $K_2[RuCl_5(H_2O)]$, and to have the constitution (A). The material was prepared according to Goremykin's procedure [1] and had the same measured properties as his product. However, there were



immediate difficulties in the interpretation of the observed X-ray diffraction which suggested that the constitutional formula was erroneous. Analysis for hydrogen agrees with the formula $[RuCl(NH_3)_5]Cl_2$, and is a much more sensitive test of the two formulæ than the previous analyses for other elements. An X-ray structure determination has been taken to a stage of refinement sufficient to confirm the constitution now assigned.

Crystal Data.—$[RuCl(NH_3)_5]Cl_2$, $M = 293{\cdot}2$, orthorhombic bipyramidal, $a = 13{\cdot}34 \pm 0{\cdot}03$, $b = 10{\cdot}86 \pm 0{\cdot}03$, $c = 6{\cdot}76 \pm 0{\cdot}02$, $U = 979{\cdot}3$ Å^3, $D_m = 2{\cdot}00$ (by flotation), $Z = 4$, $D_c = 1{\cdot}989$, $F(000) = 580$, $\mu = 206$ cm.$^{-1}$. Space group *Pnma* (D_{2h}^{16}, No. 62). Cu-K_α radiation, single-crystal oscillation and Weissenberg photographs. Optically biaxial.

Structure.—The intensities were estimated visually from Weissenberg films obtained by the multiple-film technique. Lorentz and polarisation corrections were applied. No correction was applied for absorption but to minimise this effect small crystals (maximum dimension 0·01 mm.) were used.

Whichever formula is assumed there must be four ruthenium atoms in the unit cell. On the basis of absent reflexions alone, the space-group could be *Pnma* or $Pna2_1$. In either of these the four ruthenium atoms are related to each other by two glide-plane symmetry operations. In $Pna2_1$, where the general position is four-fold, this is not compatible with a binuclear complex. In *Pnma* four ruthenium atoms could formally occupy special positions but none of these is compatible with a binuclear complex. The three principal Patterson projections were evaluated, and were readily interpreted on the assumption of the space group *Pnma* with ruthenium atoms in the planes of symmetry and so separated as to confirm the absence of a binuclear complex. Patterson peaks of suitable height could be explained by four equivalent chlorine atoms in the plane of symmetry and eight equivalent chlorine atoms in general positions. The first four are linked to ruthenium atoms but the others are not. Fourier F_o syntheses were carried

[1] Goremykin, *Izvest. Akad. Nauk S.S.S.R., Otdel. khim. Nauk*, 1947, 427.

out phased on these approximate atomic positions and were followed by difference syntheses from which the nitrogen atoms were located and the atomic parameters refined. The observable $F(hk0)$ and $F(0kl)$ are restricted in number by systematic absences and their value for refinement of atomic parameters is limited by the overlap of atoms in the mirror plane. A least-squares refinement was carried out with partial three-dimensional data by J. S. Rollett's programme SFLS [2] on a Ferranti "Mercury" computer. This programme uses anisotropic temperature factors. The refinement resulted in improved atomic parameters. For 550 $F(hkl)$ an R value of 27·4%, given by the provisional

TABLE 1.

Observed structure amplitudes and calculated structure factors for hkl [in each set of three columns the first lists the values of h, the second $F_{obs.}$ ($\times$ 5) and the third $F_{calc.}$ ($\times$ 5)].

h 0 0			*h* 8 0			*h* 1 1			*h* 0 2			*h* 8 2			*h* 4 3		
2	303	339	4	426	−448	16	144	144	2	102	29	0	339	−253	2	125	148
4	924	−836	6	84	−79				3	1002	−937				3	47	−31
6	201	−168	8	305	309	*h* 2 1			4	833	811	*h* 12 2			5	605	538
8	532	518				1	631	−588	5	117	360	0	257	−221	6	200	−209
10	420	347	*h* 9 0			2	482	979	6	352	336				7	357	302
14	307	−302	2	474	−422	3	222	237	7	300	360	*h* 0 3			8	214	−185
16	497	−355	6	389	386	4	62	91	8	325	−205	1	257	−232	9	479	−451
			8	504	482	5	182	159	9	223	−119	2	194	221	10	88	−77
h 1 0			12	192	−253	6	488	−461	10	195	−252	3	57	−42	11	418	−396
2	820	−865				7	130	−171	11	217	−234	5	720	702	13	251	248
4	133	−129	*h* 10 0			8	71	−106	12	212	−89	6	242	−264			
6	580	535	0	467	−442	9	195	−109	13	125	−248	7	366	360	*h* 5 3		
8	751	758	2	309	−288	10	170	182	14	277	124	8	221	−227	0	312	258
12	459	−310	6	420	373	12	201	193	16	81	96	9	471	−526			
16	322	297	10	411	−475	13	145	90				11	534	−475	*h* 7 3		
									h 1 2			13	303	275	0	247	−193
h 2 0			*h* 11 0			*h* 3 1			1	237	−204	15	358	306			
0	770	−673	2	365	409	0	380	489	2	587	498				*h* 9 3		
2	400	−507	4	90	145	1	127	121	3	347	326	*h* 1 3			0	247	179
4	452	−311	6	374	−353	2	89	71	4	462	398	0	316	255			
6	560	500	8	426	−410	3	93	107	5	769	717	1	470	337	*h* 11 3		
8	153	−133				4	317	−405	6	243	−195	2	148	156	0	193	−177
10	787	−643	*h* 12 0			5	205	−180	7	94	104	3	859	686			
14	491	494	0	424	639	6	361	−346	8	151	−177	4	101	−86	*h* 0 4		
16	190	170	4	413	−358	7	328	−342	9	311	−290	6	69	−58	0	391	−335
						8	259	192	10	158	145	7	434	−419	1	681	623
h 3 0			*h* 13 0			9	279	−223	11	250	−232	8	55	51	2	152	72
2	470	540	2	272	−309	10	401	348	12	356	342	9	120	−116	3	556	563
6	474	−428				11	54	20	13	132	143	10	124	110	4	260	199
8	662	−580	*h* 0 1			14	211	−232	15	182	196	11	334	342	5	379	−325
12	288	221	1	333	340	15	59	−104	16	127	−130	13	289	328	7	526	−581
16	329	−258	2	415	−456	16	75	−95				14	109	−129	8	160	−147
			3	201	249				*h* 2 2			15	76	−74	9	189	−184
h 4 0			4	617	−688	*h* 4 1			0	275	−182				11	165	133
0	1641	1659	5	242	−208	1	239	249	1	184	−189	*h* 2 3			13	141	172
2	259	248	6	184	179	2	278	−294	3	439	393	1	493	503			
4	487	−622	7	273	−210	3	185	193	4	352	−307	3	559	−551	*h* 1 4		
8	506	430	8	662	720	4	467	−490	5	316	313	4	60	12	1	784	641
10	314	257	9	272	264	6	157	128	6	420	−396	5	548	−574	2	157	116
14	187	−261	10	158	−100	7	244	−157	7	323	−296	6	145	129	3	103	−78
16	249	−301	11	192	193	8	597	564	8	70	43	7	243	209	4	94	47
			12	556	−628	9	279	227	9	231	−234	8	172	207	5	388	−356
h 5 0			13	326	−244	10	159	−93	10	346	323	9	213	246	7	57	−45
2	631	−697	14	179	−135	11	200	158	11	375	395	10	114	121	8	82	−52
4	216	−219	15	218	−254				13	318	352	12	70	−58	9	406	409
6	519	518	16	251	310	*h* 5 1			14	210	−166	14	62	34	10	83	58
8	753	687				0	534	−684	15	138	−138				11	280	226
			h 1 1									*h* 3 3			12	74	64
h 6 0			0	720	−829	*h* 7 1			*h* 3 2			0	257	−185	13	219	−210
0	614	−619	1	259	−197	0	467	416	1	546	116	1	282	−239	15	122	−324
2	443	−411	2	183	−136				2	328	−328	2	128	−125			
6	530	501	3	220	−189	*h* 9 1			3	256	−279	3	528	−511			
10	618	−620	4	619	591	0	524	−419	4	327	−286	4	84	29	*h* 2 4		
14	458	488	5	209	212				5	511	−550	7	316	324	0	91	−53
			6	511	478	*h* 11 1			6	137	117	8	52	−38	1	130	−109
h 7 0			7	430	404	0	424	358	7	64	−66	9	77	68	3	228	−210
2	445	474	8	249	−240				8	114	98	10	55	−65	4	99	91
6	368	−405	9	303	258	*h* 13 1			9	226	226	11	271	−303	5	157	−81
8	515	−492	10	547	−446	0	338	−307	10	126	−134	13	292	−261	6	151	−168
12	205	226	11	58	−30				11	208	176	14	113	96	7	472	488
			12	59	−49	*h* 0 2			12	270	−278	15	63	82	9	382	380
h 8 0			13	58	−43	0	459	−502	13	119	−120				10	216	208
0	859	924	14	298	286	1	701	−664	14	96	−111	*h* 4 3			11	236	−222
2	184	189	15	96	101				15	151	−155	1	179	−155	13	168	−193
									16	84	103						

[2] Mills and Rollett, "Computing Methods and the Phase Problem in X-Ray Crystal Analysis," Pergamon Press, London, 1961, p. 107.

TABLE 1. (*Continued*).

h 3 4			*h* 0 5			*h* 3 5			*h* 1 6			*h* 4 6			*h* 3 7		
1	501	−501	13	162	−173	11	145	169	2	376	−329	4	416	−458	3	52	27
2	151	−132				12	141	57	3	62	134	5	83	−92	4	268	−282
3	47	41	*h* 1 5						4	193	−198	6	199	−129	6	152	−183
4	49	−45	0	528	423	*h* 4 5			5	216	222	7	76	103			
5	256	245	1	335	−282	1	268	260	6	262	208	8	150	167	*h* 4 7		
6	52	33	2	183	122	3	61	−73	7	60	69	9	45	49	2	165	−204
8	55	45	3	366	−321	4	127	132	8	205	217	11	84	−153	3	72	77
9	349	−323	4	170	−131	5	196	−312	9	176	−151				4	240	−250
10	76	−61	5	58	60	6	124	−91	10	158	−84	*h* 8 6			6	85	116
11	176	−166	6	173	−128	7	129	−131	11	727	−127	0	484	346			
12	66	−67	7	337	332	8	405	−408	12	124	−272				*h* 5 7		
13	153	183	8	83	121	9	311	273				*h* 0 7			0	366	−260
			9	191	133	10	52	−58	*h* 2 6			1	125	−159			
h 4 4			10	201	184	11	181	176	1	169	150	2	233	−245	*h* 7 7		
0	254	−279	11	207	−214	12	194	208	2	114	−92	3	113	101	0	243	208
1	519	485	12	61	−41				3	221	170	4	292	−300			
2	76	54	13	146	−225	*h* 5 5			4	123	155	6	102	146	*h* 0 8		
3	468	443				0	510	381	6	338	342	8	399	291	0	385	−341
4	210	197	*h* 2 5						7	74	−62				1	197	−172
5	362	−296	1	422	−299	*h* 7 5			9	165	42				2	139	−134
6	60	−51	2	456	−444	0	394	−303	10	218	−315	*h* 1 7			3	139	−122
7	484	−482	3	189	179				11	67	101	0	207	−234	4	199	230
8	88	−133	4	111	90	*h* 9 5						1	54	22			
9	158	−140	5	275	250	0	361	289	*h* 3 6			2	54	−78	*h* 1 8		
11	117	104	6	302	366				1	55	35	4	331	335	1	186	−64
13	118	126	8	166	130	*h* 0 6			2	293	279	6	237	232	4	108	121
			9	197	−184	0	478	495	3	150	−98	7	46	−61			
h 8 4			11	66	−94	1	156	−135	4	181	156	8	120	−123	*h* 2 8		
0	257	−193				3	273	−222	5	200	−157				0	159	208
			h 3 5			4	428	−529	6	168	−181	*h* 2 7			2	70	118
h 0 5			0	366	−364	5	115	−104	7	49	−59	1	68	−42			
1	342	346	1	237	211	6	184	−161	8	147	−171	2	349	368	*h* 3 8		
4	130	152	2	142	−117	7	138	149	9	117	104	4	144	136	2	135	−168
5	363	−385	3	295	233	8	179	179	10	53	87	5	66	59	3	52	−60
6	131	−91	4	108	107	10	162	128	11	59	95	6	159	−223			
7	180	−164	6	78	110	11	138	−184	*h* 4 6						*h* 4 8		
8	402	−466	7	244	−247				0	373	429	*h* 3 7			0	179	−288
9	324	337	8	76	−120	*h* 1 6			1	87	−95	0	185	180			
11	203	221	9	120	−88	1	84	−96	3	192	−173	2	48	55			
12	272	232	10	145	−169												

TABLE 2.

Atomic co-ordinates and standard deviations (σ).

	x		*y*		*z*	
Ru	0·103	0·0009	0·25	0·00	0·180	0·0019
Cl_1	0·474	0·0027	0·25	0·00	0·554	0·0074
Cl_2	0·146	0·0023	−0·001	0·0032	0·659	0·0046
N_1	0·002	0·0062	0·25	0·00	0·412	0·010
N_2	0·208	0·0060	0·25	0·00	0·962	0·011
N_3	0·226	0·0056	0·25	0·00	0·385	0·0074
N_4	0·101	0·0064	0·056	0·0038	0·193	0·0039

TABLE 3.

Thermal parameters (all units 10^{-3} Å^2).

	B_{11}	B_{22}	B_{33}	B_{23}	B_{13}	B_{12}		B_{11}	B_{22}	B_{33}	B_{23}	B_{13}	B_{12}
Ru	1·1	0·3	6·6	0	−1·1	0	N_1	11	13	20	0	6	0
Cl_1	1·2	2·7	16·6	0	5·2	0	N_2	11	17	22	0	2	0
Cl_2	3·3	4·7	11·0	−1·6	1·2	0·8	N_3	10	22	8	0	1	0
							N_4	1	9	4	−4	3	−2

TABLE 4.

Interatomic distances (Å) with their standard deviations (σ), and some bond angles.

Ru–Cl_1	2·34	0·05	Cl_1–Ru–N_4	90·9°	N_1–Ru–N_3	89·1°
Ru–N_1	2·07	0·09	Cl_1–Ru–N_2	89·9	N_3–Ru–N_2	89·4
Ru–N_2	2·09	0·09	Cl_1–Ru–N_3	179·3	N_1–Ru–N_4	87·7
Ru–N_3	2·11	0·08	Cl_1–Ru–N_1	91·6	N_2–Ru–N_4	93·3
Ru–N_4	2·11	0·04	N_4–Ru–N_4	175·5		

parameters deduced from projections only, was refined to 16·9% but could not be further reduced. Calculated standard deviations for interatomic distances lying in the plane of symmetry are higher than were expected. Attempts to improve them by refinement

based on the assumption of space group $Pna2_1$, in which the atoms are not restricted to positions in this plane, were unsuccessful. The agreement already obtained shows that the atomic positions cannot differ greatly from those tabulated. It is possible that some form of disordered structure might give an improved agreement factor; there is no direct evidence of disorder and such structures have not been considered in detail. Table 1 gives the observed and calculated structure factors. The atomic scattering factors for chlorine and nitrogen were taken from Berghuis *et al.*[3] For ruthenium(III) the values given by Thomas and Umeda [4] were used with a correction for anomalous dispersion.[5]

Atomic co-ordinates with standard deviations are listed in Table 2 and thermal parameters in Table 3. The standard deviations are minimum values since they were obtained from a set of normal equations derived on the assumption that changes in co-ordinates of one atom do not affect the co-ordinates of the others. Some bond lengths and angles are given in Table 4. The analysis is considered accurate enough to establish the chemical constitution. The compound is structurally similar (distorted fluorite type) to others [6] of general formula $[MA_5B]X_2$, including $[Rh(NH_3)_5Cl]Cl_2$.[7] The ruthenium complex has nearly regular octahedral bonds. The Ru–Cl distance 2·34 Å is comparable with Mathieson, Mellor, and Stephenson's [8] 2·36 in $Ru_2Cl_{10}O$. For Ru–N there is no comparable measurement in an ammine. The values, between 2·07 and 2·11, are reasonable when compared with similar distances in related compounds.

The compound is presumably produced by autoxidation of hydrazine, apparently catalysed by some species such as Ru(III) in solution. In support of this is the observation that the gas evolved in the reaction is nitrogen, not hydrogen chloride as reported. This possibility of autoxidation, which should be taken into account in the preparation of hydrazine complexes generally, may perhaps be turned to advantage when the desired product is an ammine.

Experimental.—The material was prepared by Goremykin's method and consisted of small yellow-brown distorted octahedra, as described. The two principal refractive indices readily accessible by immersion methods were 1·69 and 1·72, as measured approximately with the light transmitted from a tungsten-filament lamp. Goremykin gives 1·684, 1·72 for an unstated wavelength. The magnetic moment, 2·07 B.M., is the same as that listed by Goremykin if allowance is made for the different formula that he uses. It corresponds to one unpaired electron per ruthenium atom and does not distinguish between the two formulæ. The prepared sample gave an *X*-ray powder diffraction pattern identical with that of an authentic specimen of the *complex* $[Ru(NH_3)_5Cl]Cl_2$ prepared by a method that did not involve the use of hydrazine. The same two samples gave solutions with identical absorption spectra (Found: Ru, 34·7; N, 24·3; H, 5·3; Cl, 35·8. $[Ru(NH_3)_5Cl]Cl_2$ requires Ru, 34·4; N, 23·9; H, 5·1; Cl, 36·3. Calc. for $Ru_2(N_2H_4)_{10}Cl_8$: Ru, 35·3; N, 24·3; H, 3·5; Cl, 36·9%).

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[3] Berghuis, Haanappel, Potters, Loopstra, MacGillavry, and Veenendaal, *Acta Cryst.*, 1955, **8**, 478.
[4] Thomas and Umeda, *J. Chem. Phys.*, 1957, **26**, 293.
[5] Dauben and Templeton, *Acta Cryst.*, 1955, **8**, 841.
[6] Wykoff, "Crystal Structures," Interscience Publ., Inc., New York, 1948—1960, Vol. III.
[7] West, *Z. Krist.*, 1935, **91**, 181.
[8] Mathieson, Mellor, and Stephenson, *Acta Cryst.*, 1952, **5**, 185.