$RbCrCl_3$ ($E \parallel c$) with a crystal 0.025 cm thick, the intensity does not alter rapidly. However, this apparent discrepancy may be the result of the differences in overlap between overlapping bands in the more intense and less intense spectra.

The other anomaly is for $RbCrCl_3$ with $E \perp c$, where a quite substantial fairly broad peak at 18 080 cm^{-1} appears suddenly as the temperature is raised from 60 to 80 K but disappears by 140 K (Figure 5). A much weaker peak in the same position with the same temperature dependence is also visible with $E \parallel c$.

Discussion

Assignments. Two relevant calculations are available, both using the approximation of octahedral symmetry. Konig and Kremer[6] have presented graphically the results of the calculation of the energy levels of d^4 and d^6 systems including spin–orbit interaction while McPherson et al.[4] have assigned the spectrum of $CsCrCl_3$ on both strong-field and weak-field models, but excluding spin–orbit effects. The most obvious drawback of the second approach is that the strong band at 23 250 cm^{-1} is unassigned (weak field) or assigned to a quintet–singlet transition (strong field). We have reexamined this calculation, using as they did the weak-field matrices of Ferguson, Guggenheim, and Krausz.[7] It is clear that the assignment of the 11 600-cm^{-1} band as the $^5E \rightarrow {}^5T_2$ transition of the 6500-cm^{-1} band $^5E \rightarrow {}^3T_1(a)$ excitation must be correct. This immediately gives the value of $10Dq$ as $\sim$11 600 cm^{-1}. Either by following McPherson,[4] using 90% of the free-ion term energies, or with $B = 570$ cm^{-1}, $C = 3400$ cm^{-1}, four bands in the range 15 800–18 800 cm^{-1} can be fitted fairly well to the transitions: $^3T_1(b)$ (15 786 cm^{-1}), $^3E(a)$ (16 440 cm^{-1}), $^3T_2$ (17 982 cm^{-1}), and $^3A_1$ (18 730 cm^{-1}).

It has become apparent from the present work, however, that the 15 800–19 000-cm^{-1} region is considerably more complex than was previously known, and the assumption of only four transitions in this region is not necessarily correct. Also, the spin–orbit calculations[6] show that the $^3T_1(a)$ and $^5T_2$ manifolds are hardly split by spin–orbit interaction but that the 15 000–20 000-cm^{-1} region becomes very complex, sufficiently so to account for the transitions observed. Parameter values $Dq = 1150$ cm^{-1}, $B = 800$ cm^{-1}, and $C = 3200$ cm^{-1} with the peak field model produce the following values (cm^{-1}): $^3T_1(a)$, 6574; $^5T_2$, 11 500; $^3T_1(b)$, 15 862; $^3E(a)$, 16 724; $^3T_2$, 18 298; $^3A_1$, 20 000; $^3A_2$, 20 029; $^3E(b)$, 23 031. This is our view gives the most satisfactory agreement possible in this very simple approximation, providing an assignment of the 23 000-cm^{-1} peak to $E \rightarrow {}^3E(b)$, with three absorptions between 15 900 and 18 300 cm^{-1}. For any further progress, both spin–orbit coupling and the C_{3v} site symmetry would need to be considered, but given the degree of resolution in our spectra, little unambiguous progress can be made.

Temperature Dependence. While the various intercombination bands display enhanced intensity as has been observed in other magnetically coupled ABX_3 systems, there is only a slight dependence of intensity on temperature (with one or two exceptions). This is in contrast to the results obtained for $CsMnBr_3$[8] and $(CH_3)_4NMnBr_3$.[9] The two exceptions are the manifold at 18 080 cm^{-1} in the spectrum of $RbCrCl_3$ and the peak at 16 670 cm^{-1} in $RbCrCl_3$. The 18 080-cm^{-1} band does not appear until $\sim$60 K and disappears by 140 K. On the basis of earlier experience[1,8,9] we may conclude that this transition is magnon "hot band" assisted but we note that it is surprisingly broad. The second strikingly temperature-dependent feature, the 16 670-cm^{-1} band, is relatively intense at 4.2 K yet is nonexistent at 40 K. It appears that this peak is the 0 → 0, no-phonon origin of the manifold to its high energy side which is comprised of an $\sim$100-cm^{-1} progression of symmetric phonons. The maximum at $\sim$16 935 cm^{-1} which does not fall in this progression may be a component of a second symmetric progression of $\sim$250 cm^{-1} as might the ill-resolved, high-energy shoulder of the band located at 17 220 cm^{-1}. The temperature dependence of the 16 670-cm^{-1} origin is then due to thermal broadening by the contributions of phonon hot bands. This seems to be borne out by the red shift observed in the low-energy absorption edge between 4.2 and 40 K.

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Registry No. $CsCrCl_3$, 13820-84-3; $RbCrCl_3$, 13820-90-1.

References and Notes

(1) Part 5: C. F. Putnik, G. M. Cole, and S. L. Holt, *Inorg. Chem.*, **15**, 2135 (1976).
(2) On leave from the Department of Molecular Sciences, University of Warwick, Coventry CV4 7AL, England.
(3) For a general survey of these effects, see J. F. Ackerman, G. M. Cole, and S. L. Holt, *Inorg. Chim. Acta*, **8**, 323 (1974).
(4) G. L. McPherson, T. J. Kistenmacher, J. B. Folkers, and G. D. Stucky, *J. Chem. Phys.*, **57**, 3771 (1972).
(5) G. N. Tischemko, *Tr. Inst. Kristallogr., Akad. Nauk SSSR*, **11**, 93 (1955).
(6) E. Konig and S. Kremer, *J. Phys. Chem.*, **78**, 56 (1974).
(7) J. Ferguson, J. H. Guggenheim, and E. R. Krausz, *Aust. J. Chem.*, **22**, 1809 (1969).
(8) G. M. Cole, C. F. Putnik, and S. L. Holt, *Inorg. Chem.*, **14**, 2219 (1975).
(9) C. F. Putnik, G. M. Cole, and S. L. Holt, *Inorg. Chem.*, **15**, 2001 (1976).
(10) H. J. Seifert and K. Klatyk, *Z. Anorg. Allg. Chem.*, **334**, 113 (1964).

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Synthesis and Some Crystal Data of H_xReO_3 ($x = 0.15$)

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Rhenium trioxide is known as a chemically stable compound in air at room temperature.[1] Unidentified x-ray diffraction peaks, however, were found after 1 h of grinding an ReO_3 powder sample in guaranteed reagent grade ethyl alcohol in an agate mortar and they became bigger and clearer with the length of grinding time. While grinding in carbon tetrachloride (guaranteed reagent grade) for 4 h at room temperature yielded no diffraction peaks other than those of ReO_3, the clearly split diffraction peaks from those of ReO_3 were seen in the case of grinding in distilled water for 0.5 h. The above experiments suggested that some chemical reaction of ReO_3 powder with water occurred in the grinding process at room temperature, so we boiled ReO_3 powder in water at 100 °C for several hours and obtained a new compound.

The chemical composition was determined to be H_xReO_3 ($x = 0.15 \pm 0.04$) by means of mass spectroscopy and thermogravimetric analysis (tga).

The purpose of the present paper is to report the synthesis and some crystal data of H_xReO_3.

Experiments and Results

(A) Sample Synthesis. Re metal powder (99.99% purity, Herman C. Stark, Berlin) was employed as a starting material, and ReO_3 was synthesized and identified as a single phase by x-ray diffraction studies.[2] The ReO_3 thus obtained was ground under distilled water in an agate mortar for about 10 h, and 2–3 g of ReO_3 was boiled with about 300 ml of water in a Pyrex glass vessel. The change of the boiling time from 5 h to 1 week did not bring about any change in *d* spacings and relative intensities of x-ray diffraction peaks of the synthesized compound. The gold-colored compound obtained was elec-

Table I. *Q* Values ($Å^{-2}$) and Relative Intensities of H_xReO_3 ($x = 0.15$)

hkl	d_{obsd}^{-2}	d_{calcd}^{-2}	*I*	*hkl*	d_{obsd}^{-2}	d_{calcd}^{-2}	*I*
100	0.070 46	0.070 36	100	023	0.940 96	0.940 90	3
010	0.071 21	0.071 36	90	321	0.991 49	0.991 52	4
001	0.072 69	0.072 83	50	312	0.996 01	0.996 53	4
110	0.141 68	0.141 72	50	231	0.996 36	0.996 53	4
101	0.142 91	0.143 19	70	132	1.003 58	1.003 93	5
011	0.144 27	0.144 19	40	213	1.008 29	1.008 25	5
111	0.214 32	0.214 55	28	123	1.011 00	1.011 26	4
200	0.281 04	0.281 44	16	400	1.126 69	1.125 76	1
020	0.285 15	0.285 45	20	040	1.141 87	1.141 80	1
002	0.290 82	0.291 31	10	004	1.165 79	1.165 24	1
210	0.352 72	0.352 80	20	410	1.197 43	1.197 12	2
201	0.354 35	0.354 27	30	401	1.198 92	1.198 59	2
120	0.355 38	0.355 81	32	322	1.210 06	1.210 00	4
021	0.358 10	0.358 28	22	140	1.212 20	1.212 16	5
102	0.361 57	0.361 67	24	041	1.215 03	1.214 63	7
012	0.362 61	0.362 67	16	232	1.215 50	1.215 02	7
211	0.425 41	0.425 63	16	223	1.221 59	1.222 34	5
121	0.428 04	0.428 64	24	104	1.234 85	1.235 60	2
112	0.432 79	0.433 03	12	014	1.236 31	1.236 60	2
220	0.566 84	0.566 89	7	411	1.269 07	1.269 95	2
202	0.572 57	0.572 75	9	330	1.275 25	1.275 51	2
022	0.576 14	0.576 76	8	141	1.284 98	1.284 99	4
300	0.633 01	0.633 24	2	303	1.288 58	1.288 69	3
221	0.639 77	0.639 72	10	033	1.297 90	1.297 71	2
030	0.642 56	0.642 26	14	114	1.307 15	1.306 96	2
212	0.643 37	0.644 11	14	331	1.348 34	1.348 33	2
122	0.646 92	0.647 12	13	313	1.359 87	1.360 05	3
003	0.655 02	0.655 45	2	133	1.367 68	1.368 07	3
310	0.705 32	0.704 60	4	420	1.410 35	1.411 21	1
301	0.706 43	0.706 07	4	402	1.417 38	1.417 07	2
130	0.712 32	0.712 62	5	240	1.423 55	1.423 24	3
031	0.714 97	0.715 09	5	042	1.433 20	1.433 11	2
103	0.725 50	0.725 81	4	204	1.447 08	1.446 68	2
013	0.726 90	0.726 81	4	024	1.451 41	1.450 69	1
311	0.776 73	0.777 43	4	421	1.483 95	1.484 04	3
131	0.784 97	0.785 45	5	412	1.489 06	1.488 43	3
113	0.797 07	0.797 17	4	241	1.496 31	1.496 07	7
222	0.857 90	0.858 20	6	142	1.503 80	1.503 47	6
320	0.918 11	0.918 69	2	214	1.518 58	1.518 04	3
230	0.923 58	0.923 70	5	124	1.521 31	1.521 05	2
302	0.925 43	0.924 55	3	332	1.566 75	1.566 81	3
032	0.933 48	0.933 57	3	323	1.574 11	1.574 14	5
203	0.936 75	0.936 89	4	233	1.579 40	1.579 15	3

Table II. Lattice Constants of ReO_3 and H_xReO_3 ($x = 0.15$)

Compd	Lattice const at room temp, Å
H_xReO_3	$a = 3.7700 \pm 0.0002$ $b = 3.7434 \pm 0.0002$ $c = 3.7056 \pm 0.0002$
ReO_3 (starting compd)	$a = 3.7477 \pm 0.0001$
ReO_3 (obtained from H_xReO_3)	$a = 7.4958 \pm 0.0002$
ReO_3[5]	$a = 3.748$

trically conductive, was insoluble in hydrochloric acid and dilute sodium hydroxide, but was soluble in nitric acid at room temperature.

(B) Determination of Chemical Composition. The procedures of chemical analysis applied to the obtained compound are as follows.

(1) The sample thus synthesized was dried under vacuum (10^{-3} mmHg) at 75 °C for 1 week and kept in a desiccator for 1 day. The choice of water absorption agent, silica gel or P_2O_5, did not affect the results of the following chemical analysis.

(2) About 100 mg of sample was placed in an evacuated system (10^{-7} mmHg) with constant pumping speed for several hours and then heated to 330 °C at the rate of 10 °C/min.

Masses of the evolved gas species from the solid phase were identified by the quadrupole type mass analyzer and the pressure in the system was also simultaneously observed. Gas evolution from the solid sample began at about 175 °C and only H_2O molecules were detected in the gas phase. At about 330 °C the degassing process finished. The difference between the initial sample weight and the final one was determined to be 0.40% using a Sartorius microbalance. In addition, the quantity of evolved gas estimated from the weight loss measurement was ascertained through the integration of the pressure change in the evacuated system on the basis of the constant pumping speed. Tga indicated that the vaporization of ReO_3 was negligibly small between room temperature and 330 °C at 10^{-6} mmHg.

The residual solid was identified to be a single phase with a superlattice of $2 \times a_{ReO_3}$, where a_{ReO_3} is the lattice constant of starting ReO_3.

(3) The residual solid was heated again to 250 °C in air and relative weight gain was determined to be 0.38%, showing that the residual solid was an oxygen-deficient rhenium trioxide phase.

(C) Heat Treatment of the Sample under 1 Atm. (1) About 2500 mg of the sample obtained in (A) was heated at 95 ± 3 °C for 1 day and was changed to single phase ReO_3 with 0.07% relative weight loss measured with a Mettler H-20 balance. The sample was heated at 150 ± 5 °C in flows of dried H_2 and N_2 during one night. No chemical reaction was observed in either case.

(2) ReO_3 powder (particle size 1–3 μm) was put in dried H_2 gas with a flow rate of about 1 cm^3/s and was converted to the hydrogen-containing compound H_xReO_3, whose x-ray diffraction pattern was crystallographically identical with that of the specimen obtained in process A.

Although the splitting of the diffraction peaks was much less than in the case of boiled ReO_3 in H_2O, the distortion from cubic symmetry was clear.

(D) X-Ray Powder Diffractometry at Room Temperature. X-ray powder diffraction using a scintillation counter diffractometer (Ni-filtered Cu Kα radiation and Si standard) revealed that the sample obtained was of single phase; every *d* spacing could be easily indexed based on an orthorhombic unit cell. Indexed d_{obsd}^{-2}, d_{calcd}^{-2}, and relative intensities are listed in Table I and crystal data are shown in Table II.

The de Wolff M_{20} value, one of the figures of merit for an indexed diffraction pattern, was 66.2 ($Q_{20} = 0.5668$, $\bar{\epsilon} = 0.000214$, and $N_{20} = 20$).[3,4]

From the above results, we could determine the new compound as H_xReO_3 ($x = 0.15 \pm 0.04$). Hydrogen in this compound reacts with oxygen in air at 95 °C to yield H_2O gas. On the other hand, at 10^{-7} mmHg, H_2O gas was evolved from solid-phase H_xReO_3 at 175 °C, leaving oxygen-deficient rhenium trioxide, whose lattice constant was twice that of starting ReO_3.

In the near future we will report the structure analysis of single-crystal H_xReO_3 and will discuss the relation between the hydrogen content and the crystal distortion.

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References and Notes

(1) R. D. Peacok, "Comprehensive Inorganic Chemistry", Vol. 3, Pergamon Press Ltd., Oxford, England, 1975, pp 905–978.
(2) L. F. Audrieth, *Inorg. Synth.*, **3**, 186–187 (1950).
(3) P. M. deWolff, *J. Appl. Crystallogr.*, **1**, 108 (1967).
(4) H. Lipson and H. Steeple, "Interpretation of X-Ray Powder Diffraction Patterns", Macmillan, London, 1967, pp 155–156.
(5) McIlvried and McCarthy, "Powder Diffraction Line", Joint Committee on Powder Diffraction Standards, 1975, File No. 24-1009.