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Low-temperature heat capacities of three molybdenum oxychlorides [a]

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The heat capacities of MoO_2Cl_2, $McOCl_3$, and $MoOCl_4$ have been determined from 5 to 350 K. No thermal anomalies were detected over this temperature range. At 298.15 K the values of the heat capacity C_p, entropy $S°$, and the function $\{G°(T) - H°(0)\}/T\}$ found were (for MoO_2Cl_2), 24.53, 32.42, and -16.71 $kcal_{th}\ K^{-1}\ mol^{-1}$; (for $MoOCl_3$), 26.85 39.16, and -20.94 $kcal_{th}\ K^{-1}\ mol^{-1}$; and (for $MoOCl_4$), 33.44, 48.28, and -25.80 $kcal_{th}\ K^{-1}\ mol^{-1}$. The derived functions stated above assume the extrapolation of the observed results from 0 to 5 K to follow the Debye limiting law; *i.e.*, possible magnetic thermal anomalies below 5 K have not been included.

1. Introduction

In conjunction with already reported studies on the molybdenum halides,[(1)] data on the most important oxyhalides—which so complicate the dry and wet chemistry of molybdenum—are a desiderata. Although it was anticipated that the magnetic and/or ordering contributions of these compounds might provide interesting features in the heat capacity, since none were detected over the range of investigation, it is hoped that extensions to both higher and lower temperatures may eventually be undertaken. However, higher-temperature studies will probably require a silica-lined calorimeter.

2. Experimental

SAMPLE PROVENANCE

Three oxyhalide samples, together with analytical data, were kindly provided by the Climax Molybdenum Company of Michigan. The MoO_2Cl_2 was of a yellowish color, the $MoOCl_3$ was dark brown, and the $MoOCl_4$ was dark green. The analytical information is presented in table 1. In addition, infra-red analysis on Nujol mulls revealed the proper absorption bands and the absence of water. Extra care had to be

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TABLE 1. Analytical data on molybdenum dioxodichloride, oxytrichloride, and oxytetrachloride; w denotes mass fraction and n amount of substance

Compound	10^2w(Mo) Found	10^2w(Mo) Theor.	10^2w(Cl) Found	10^2w(Cl) Theor.	10^2w(O) [a] Found	10^2w(O) [a] Theor.	n(O)/n(Mo) Found	n(Cl)/n(Mo) Found
MoO_2Cl_2	48.58	(48.25)	35.29	(35.66)	16.13	(16.09)	1.99	1.96
$MoOCl_3$	43.68	(43.95)	47.96	(48.72)	8.13	(7.33)	1.11	2.95
$MoOCl_4$	37.99	(37.81)	54.83	(55.89)	7.18	(6.30)	1.10	4.0

[a] By difference.

taken in loading the oxyhalides because of their very high sensitivity to moisture, and particularly with the oxytetrachloride which is also light sensitive. Sample masses, densities, molar masses, and amounts of helium gas used to enhance thermal equilibration within the calorimeter are summarized in table 2.

TABLE 2. Sample and experimental details (Torr = (101325/760) Pa)

Compound	M/g mol^{-1}	m/g	ρ/g cm^{-3}	p(He)/Torr
MoO_2Cl_2	198.8458	21.5629	3.168 [a]	65
$MoOCl_3$	218.2984	41.2239	3.151 [b]	62
$MoOCl_4$	253.7515	41.6108	3.135 [c]	93.5

[a] Calculated on the assumption that it is isostructural with WO_2Cl_2.
[b] Reference 2.
[c] Estimated.

APPARATUS

Heat-capacity measurements were made in the Mark II adiabatic cryostat which has been described previously.[(3)] The samples were contained in a gold-plated copper calorimeter (laboratory designation W-48) which incorporates a gold-gasketed screw-closure, gold-plated copper vanes to enhance conductivity, mass 33.4657 g, internal volume 44.44 cm^3. To facilitate rapid thermal equilibration, small amounts of helium gas were introduced. The temperature of the calorimeter was measured with a platinum capsule-type (nominal) 25 Ω resistance thermometer (laboratory designation A-5) inserted into a re-entrant well in the calorimeter. The temperature scale was judged to correspond to the IPTS–1968 to within 0.03 K from 10 to 90 K and within 0.04 K from 90 to 350 K. A 150 Ω constantan heater, wound non-inductively on a cylindrical gold-plated-copper heater sleeve surrounds the resistance thermometer. Accuracy is assured by ultimately referring all determinations of mass, temperature, resistance, and potentials to calibrations performed by the National Bureau of Standards and by the measurement of heat capacity of standards established by the Calorimetry Conference.[(4)]

3. Results and discussion

HEAT CAPACITY

The measured heat capacities of the three oxyhalides are presented in table 3 and depicted in figure 1. The results are presented in chronological sequence so that the magnitude of the temperature increments employed may usually be inferred from the

TABLE 3. Heat capacities of molybdenum dioxodichloride, oxytrichloride, and oxytetrachloride

(cal_{th} = 4.184 J)

T/K	$C_p/cal_{th}\,K^{-1}\,mol^{-1}$	T/K	$C_p/cal_{th}\,K^{-1}\,mol^{-1}$	T/K	$C_p/cal_{th}\,K^{-1}\,mol^{-1}$
Molybdenum dioxodichloride (MoO_2Cl_2)					
Series I		5.91	0.062	52.36	7.331
56.83	8.009	6.74	0.103	59.10	8.357
63.88	9.047	7.72	0.166	65.51	9.267
72.57	10.16	8.73	0.246		
81.82	11.35	9.64	0.334	Series III	
92.14	12.54	10.79	0.453	208.23	21.32
103.18	13.68	12.46	0.648		
113.71	14.76	14.16	0.860	Enthalpy detn. A	
124.28	15.80	15.44	1.057	218.60	21.82
135.41	16.82	16.59	1.222	228.82	22.29
146.80	17.76	17.73	1.386	238.90	22.73
158.13	18.58	18.97	1.575	248.86	23.14
169.11	19.28	20.51	1.824	258.72	23.46
179.83	19.90	22.48	2.142	268.87	23.77
190.64	20.46	24.89	2.564	279.59	24.07
201.49	20.98	27.76	3.069	291.23	24.35
212.15	21.50	31.09	3.677	303.51	24.61
222.64	22.00	35.14	4.428	315.67	24.91
		39.51	5.192	327.73	25.32
Series II		42.75	5.712	340.36	25.60
5.04	0.028	46.30	6.344		
Molybdenum oxytrichloride ($MoOCl_3$)					
Series I		212.72	24.50	Series III	
55.57	9.680	223.54	24.96	4.129	0.115 [a]
60.81	10.66			4.426	0.104
67.95	11.90	Series II		4.821	0.102
75.64	13.10	210.35	24.32	5.277	0.216
83.13	14.27	221.21	24.80	6.046	0.222 [a]
91.85	15.48	231.94	25.12	6.734	0.479 [a]
102.17	16.72	243.14	25.49	7.481	0.610 [a]
113.48	17.98	254.79	25.85	8.426	0.882 [a]
124.83	19.14	266.33	26.15	9.517	1.218 [a]
135.59	20.13	277.76	26.38	10.92	1.141 [a]
146.44	20.97	289.07	26.65	12.53	1.293
157.45	21.73	300.26	26.87	13.92	1.529
168.13	22.37	311.95	27.16	15.12	1.757
179.15	22.97	324.14	27.40	16.25	1.920
190.56	23.50	336.25	27.61	17.46	2.150
201.73	24.04	347.54	27.69	18.92	2.402

TABLE 3—*continued*

$\frac{T}{\text{K}}$	$\frac{C_p}{\text{cal}_{\text{th}}\,\text{K}^{-1}\,\text{mol}^{-1}}$	$\frac{T}{\text{K}}$	$\frac{C_p}{\text{cal}_{\text{th}}\,\text{K}^{-1}\,\text{mol}^{-1}}$	$\frac{T}{\text{K}}$	$\frac{C_p}{\text{cal}_{\text{th}}\,\text{K}^{-1}\,\text{mol}^{-1}}$
		Molybdenum oxytrichloride ($MoOCl_3$) (cont.)			
20.84	2.759	5.89	0.263 [a]	10.15	1.197 [a]
23.00	3.172	6.52	0.628 [a]	10.36	1.375 [a]
25.36	3.647	6.97	0.507 [a]	10.58	1.031 [a]
27.87	4.153	7.43	0.602 [a]	11.05	1.046 [a]
30.66	4.719	7.82	0.635 [a]	11.90	1.157 [a]
34.17	5.436	8.18	0.771 [a]	12.93	1.340
38.47	6.330	8.50	0.848 [a]		
43.69	7.444	8.78	0.914 [a]	Series V	
50.38	6.776	9.05	1.019 [a]	6.39	0.436 [a]
57.45	10.03	9.29	1.072 [a]	8.55	0.906 [a]
		9.52	1.194 [a]	10.23	1.198 [a]
Series IV		9.74	1.255 [a]	11.53	1.109 [a]
4.72	0.095 [a]	9.95	1.221 [a]		
		Molybdenum oxytetrachloride ($MoOCl_4$)			
Series I		239.17	31.37	10.05	0.839
57.19	12.58	249.65	31.85	11.20	1.098
63.60	13.98	260.02	32.25	12.51	1.354
71.54	15.52	270.28	32.62	13.97	1.705
80.97	17.26			15.85	2.158
91.06	18.95	Series II		17.81	2.640
101.56	20.46	257.42	32.10	19.55	3.064
112.60	21.92	267.90	32.51	21.28	3.520
123.25	23.28	278.58	32.89	23.16	4.005
133.65	24.42	289.16	33.23	25.36	4.607
144.22	25.47	299.98	33.48	27.87	5.280
154.74	26.40	311.06	33.25 [a]	30.82	6.071
164.96	27.20			34.69	7.114
175.20	27.93	Series III		38.77	8.162
185.83	28.58	4.84	0.172	43.03	9.215
196.60	29.22	5.80	0.224	48.32	10.54
207.18	29.78	6.96	0.353	52.94	11.60
217.83	30.37	8.08	0.502	57.34	12.60
228.57	30.87	9.072	0.656	63.60	13.96

[a] Not curvature corrected and not used in final curve-fitting routine.

differences between adjacent mean temperatures of the determinations. These values are considered to have a precision—and an accuracy—expressed by a standard deviation of 8 per cent below 10 K, decreasing to 0.1 per cent above 25 K.

Several enthalpy-type determinations on the dioxodichloride over the range 175 to 205 K revealed accord with enthalpies integrated from the heat capacities to within ± 0.02 per cent.

An apparent hump in the heat capacity of the oxytrichloride at about 9.7 K is enlarged in figure 2, and is characterized by a gradual rise followed by a rapid decline in the heat capacity; no explanation for its source is evident. The total enthalpy increment from 5 to 13 K was determined by three separate series of measurements

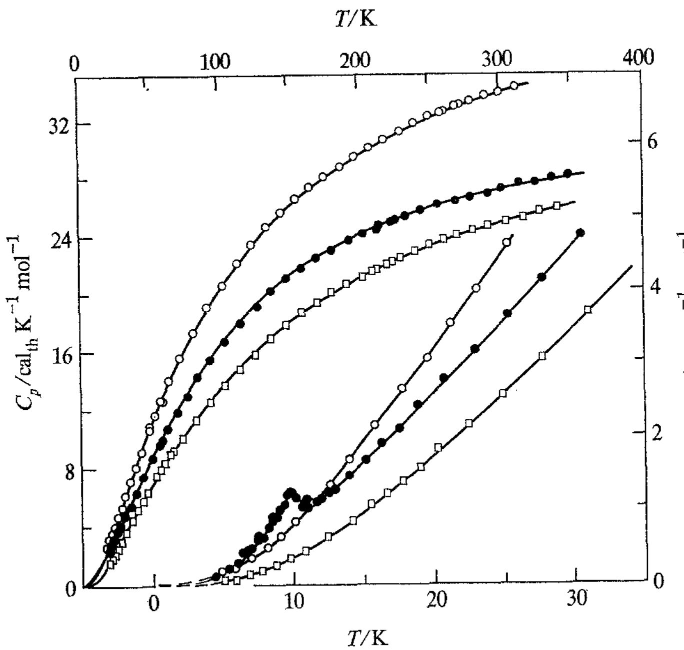

FIGURE 1. Heat capacities of: □, molybdenum dioxodichloride; ●, oxytrichloride; ○, oxytetrachloride.

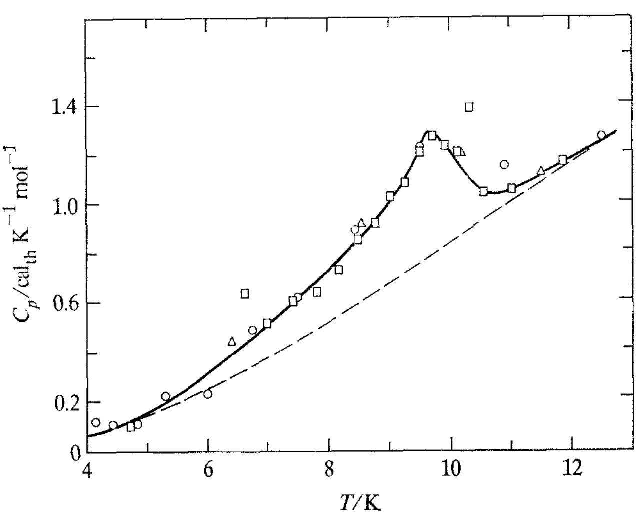

FIGURE 2. Plot of C_p against T for molybdenum oxytrichloride ($MoOCl_3$). ○, Series (II) points; □, Series III points; and .., Series IV points. The dashed line gives the lattice contribution.

as (7.0 ± 0.1) $\text{cal}_{\text{th}}\ \text{mol}^{-1}$ and deduction of the lattice contribution (6.2 ± 0.1) $\text{cal}_{\text{th}}\ \text{mol}^{-1}$ yields an enthalpy of transition 0.8 $\text{cal}_{\text{th}}\ \text{mol}^{-1}$ and a corresponding entropy of transition of 0.09 $\text{cal}_{\text{th}}\ \text{K}^{-1}\ \text{mol}^{-1}$.† The small magnitude of these values suggests it may be an impurity effect yet no transition was detected in the other oxyhalides and halides studied. It was not included in the integration of the thermodynamic functions.

The heat-capacity determinations on molybdenum oxytetrachloride were not extended higher than 310 K as the presence of an apparent exothermal reaction was detected as occurring at temperatures above 292 K. The reality of the reaction was confirmed on unloading the calorimeter when a loss of 4.6 mg (presumably copper) in the mass of the calorimeter was confirmed. Near 50 K, measurements of the heat capacity before and after the reaction gave identical values, but adjustment in the mass of the calorimeter was needed for subsequent samples.

The heat capacities below 6 K were obtained by plots of C_p/V against V^2 for these substances as shown in figure 3.

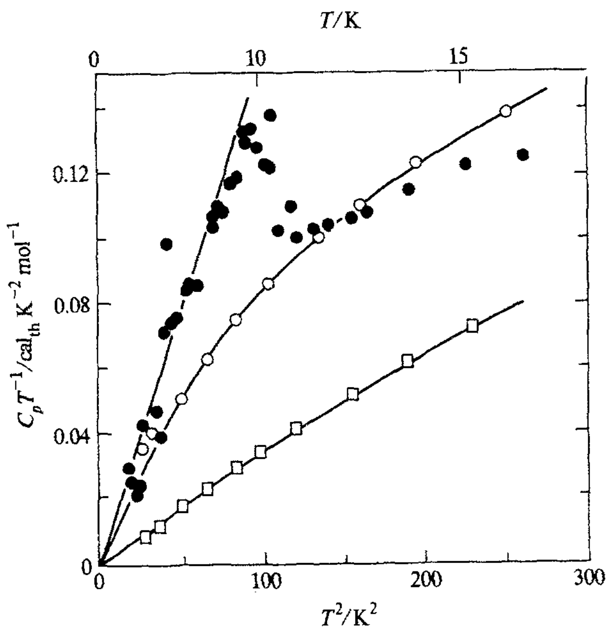

FIGURE 3. Plot of C_p/T against T^2 for: □, molybdenum dioxodichloride; ●, oxytrichloride; ○, oxytetrachloride

THERMODYNAMIC FUNCTIONS

From the results and these extrapolations, thermodynamic functions were generated and are presented in tables 4 through 6. Above 100 K these functions are probably reliable to within 0.1 per cent.

† Throughout this paper $\text{cal}_{\text{th}} = 4.184$ J.

TABLE 4. Thermodynamic functions of molybdenum dioxodichloride (MoO_2Cl_2)
(cal_{th} = 4.184 J)

T/K	C_p/cal_{th} K^{-1} mol^{-1}	$\{S°(T) - S°(0)\}$/cal_{th} K^{-1} mol^{-1}	$\{H°(T) - H°(0)\}$/cal_{th} mol^{-1}	$-\{G°(T) - H°(0)/T$/cal_{th} K^{-1} mol^{-1}
5	0.028	0.009	0.035	0.002
10	0.368	0.111	0.866	0.025
15	0.986	0.371	4.173	0.093
20	1.741	0.756	10.952	0.208
25	2.578	1.233	21.720	0.364
30	3.491	1.782	36.845	0.554
35	4.409	2.390	56.612	0.772
40	5.287	3.036	80.871	1.014
45	6.127	3.708	109.42	1.276
50	6.932	4.395	142.09	1.554
60	8.445	5.795	219.08	2.144
70	9.842	7.203	310.60	2.766
80	11.13	8.603	415.57	3.408
90	12.33	9.984	532.97	4.062
100	13.44	11.34	661.92	4.722
110	14.47	12.67	801.58	5.385
120	15.43	13.97	951.17	6.047
130	16.32	15.24	1110.0	6.705
140	17.14	16.48	1277.3	7.360
150	17.91	17.69	1452.6	8.008
160	18.61	18.87	1635.3	8.651
170	19.27	20.02	1824.7	9.286
180	19.88	21.14	2020.5	9.913
190	20.45	22.23	2222.2	10.533
200	20.97	23.29	2429.3	11.144
210	21.46	24.33	2641.6	11.748
220	21.92	25.34	2858.5	12.342
230	22.35	26.32	3079.9	12.929
240	22.74	27.28	3305.3	13.507
250	23.11	28.22	3534.7	14.076
260	23.45	29.13	3767.5	14.638
270	23.77	30.02	4003.7	15.191
280	24.06	30.89	4242.9	15.736
290	24.33	31.74	4484.8	16.274
300	24.58	32.57	4729.4	16.803
310	24.80	33.38	4976.3	17.325
320	25.02	34.17	5225.4	17.839
330	25.23	34.94	5476.7	18.345
340	25.45	35.70	5730.1	18.844
350	25.70	36.44	5985.8	19.337
273.15	23.87	30.30	4078.7	15.364
298.15	24.53	32.42	4684.0	16.706

TABLE 5. Thermodynamic functions of molybdenum oxytrichloride ($MoOCl_3$)
(cal_{th} = 4.184 J)

T / K	C_p / cal_{th} K^{-1} mol^{-1}	$\{S°(T) - S°(0)\}$ / cal_{th} K^{-1} mol^{-1}	$\{H°(T) - H°(0)\}$ / cal_{th} mol^{-1}	$-\{G°(T) - H°(0)\}/T$ / cal_{th} K^{-1} mol^{-1}
5	0.165	0.056	0.208	0.014
10	0.850	0.361	2.608	0.100
15	1.723	0.868	9.011	0.268
20	2.629	1.488	19.885	0.494
25	3.559	2.173	35.337	0.760
30	4.569	2.910	55.604	1.056
35	5.603	3.692	81.034	1.376
40	6.631	4.507	111.62	1.716
45	7.641	5.347	147.31	2.073
50	8.625	6.203	187.99	2.443
60	10.50	7.943	283.72	3.214
70	12.22	9.693	397.44	4.015
80	13.79	11.43	527.64	4.833
90	15.21	13.14	672.79	5.661
100	16.49	14.81	831.43	6.493
110	17.65	16.43	1002.2	7.323
120	18.68	18.01	1184.0	8.148
130	19.61	19.55	1375.5	8.967
140	20.45	21.03	1575.9	9.776
150	21.20	22.47	1784.2	10.57
160	21.87	23.86	1999.6	11.361
170	22.48	25.20	2221.5	12.136
180	23.03	26.50	2449.0	12.899
190	23.52	27.76	2681.8	13.648
200	23.97	28.98	2919.3	14.384
210	24.37	30.16	3161.0	15.108
220	24.75	31.30	3406.6	15.818
230	25.09	32.41	3655.8	16.515
240	25.40	33.48	3908.3	17.200
250	25.70	34.53	4163.8	17.872
260	25.97	35.54	4422.2	18.533
270	26.22	36.53	4683.2	19.181
280	26.46	37.48	4946.6	19.818
290	26.68	38.42	5212.3	20.443
300	26.89	39.32	5480.1	21.057
310	27.10	40.21	5750.1	21.661
320	27.30	41.07	6022.1	22.254
330	27.50	41.92	6296.1	22.837
340	27.69	42.74	6572.0	23.410
350	27.86	43.55	6849.8	23.974
273.15	26.30	36.83	4765.9	19.383
298.15	26.85	39.16	5430.4	20.944

TABLE 6. Thermodynamic functions of molybdenum oxytetrachloride ($MoOCl_4$)
(cal_{th} = 4.184 J)

T/K	C_p/cal_{th} K^{-1} mol^{-1}	$\{S°(T) - S°(0)\}$/cal_{th} K^{-1} mol^{-1}	$\{H°(T) - H°(0)\}$/cal_{th} mol^{-1}	$-\{G°(T) - H°(0)\}/T$/cal_{th} K^{-1} mol^{-1}
5	0.178	0.0599	0.222	0.0154
10	0.837	0.343	2.450	0.0977
15	1.947	0.884	9.317	0.263
20	3.188	1.613	22.121	0.506
25	4.503	2.464	41.317	0.811
30	5.850	3.406	67.246	1.164
35	7.175	4.407	99.818	1.555
40	8.469	5.450	138.94	1.977
45	9.723	6.520	184.44	2.422
50	10.93	7.608	236.09	2.886
60	13.19	9.803	356.86	3.856
70	15.24	11.99	499.16	4.862
80	17.09	14.15	660.95	5.889
90	18.76	16.26	840.30	6.924
100	20.27	18.32	1035.5	7.961
110	21.64	20.31	1245.1	8.994
120	22.88	22.25	1467.8	10.018
130	24.01	24.13	1702.4	11.032
140	25.04	25.95	1947.8	12.032
150	25.97	27.71	2202.9	13.019
160	26.81	29.41	2466.9	13.990
170	27.57	31.06	2738.9	14.946
180	28.25	32.65	3018.0	15.886
190	28.86	34.20	3303.6	16.809
200	29.43	35.69	3595.1	17.716
210	29.95	37.14	3892.1	18.607
220	30.45	38.55	4194.1	19.481
230	30.93	39.91	4501.0	20.340
240	31.39	41.24	4812.6	21.183
250	31.82	42.53	5128.7	22.011
260	32.24	43.78	5449.0	22.824
270	32.61	45.01	5773.3	23.623
280	32.94	46.20	6101.1	24.408
290	33.23	47.36	6432.0	25.180
300	33.49	48.49	6765.6	25.938
310	33.78	49.59	7101.8	26.683
273.15	32.72	45.38	5876.2	23.872
298.15	33.44	48.28	6703.7	25.799

It should be noted that possible magnetic-ordering transitions occurring below 5 K have not been included in the thermodynamic functions. Moreover, the values of $\{S°(T)-S°(0)\}$ and $-\{G°(T)-H°(0)\}/T$ are practical ones in that contributions from isotopic mixing have not been included.

Utilizing extant data on the enthalpies of formation on the dioxodichloride,[5] the oxytrichloride,[6] and the oxytetrachloride[7] summarized in table 7, together with entropies of oxygen[8] and chlorine[8] and the results of this research yield the standard Gibbs energies of formation shown in this table. It should be noted in both

TABLE 7. Thermodynamics of formation for molybdenum dioxodichloride, oxytrichloride, and oxytetrachloride at 298.15 K
($cal_{th} = 4.184$ J)

Compound	$\frac{-\Delta G_f^\circ}{cal_{th}\ mol^{-1}}$	$\frac{-\Delta H_f^\circ}{cal_{th}\ mol^{-1}}$	$\frac{\Delta S_f^\circ}{cal_{th}\ K^{-1}\ mol^{-1}}$
MoO_2Cl_2(c)	195.0 ± 0.9	172.1 ± 0.5	76.71 ± 0.04
$MoOCl_3$(c)	170.4 ± 0.7	148.92 ± 0.5	72.11 ± 0.04
$MoOCl_4$(c)	182.6 ± 1.3	155.87 ± 1.0	89.64 ± 0.05

the entropies and the Gibbs energies in this table that possible magnetic-ordering transitions in the oxyhalides could increase the former and decrease the latter by amounts in excess of the standard deviations noted. An endeavour to estimate the magnitude in this adjustment has been made elsewhere.[9]

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9. For supplementary material including adjuvant structural and physical properties of the substances reported in this paper and derived thermodynamics of chemical reactions made possible by the new data, order NAPS document No. 02546 for 45 pages of supplementary material. Order from ASIS/NAPS, c/o Microfiche Publications, 440 Park Avenue South, New York, N.Y. 10016, U.S.A. Remit in advance for each NAPS accession number. Make checks payable to Microfiche Publications. Photocopies are $7.25. Microfiche are $1.50. Outside of the U.S. or Canada, postage is $2.00 for a photocopy or $0.50 for a fiche.