Inorganica Chimica Acta, 36 (1979) 105–112
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Mixed-valence Effects in Tellurium–Molybdenum Oxides

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Received January 23, 1979

Powdered samples of α-Te_2MoO_7, $TeMo_5O_{16}$, α-TeO_2 and MoO_3 were studied by various spectroscopic techniques (XPS, IR, Raman, diffuse reflectance). Observed Mo($3d_{3/2}$–$3d_{5/2}$) and Te($3d_{3/2}$–$3d_{5/2}$) binding energies, combined with bond-strength bond-length calculations, indicate the presence of Te(IV) in both α-Te_2MoO_7 and $TeMo_5O_{16}$. In the latter compound some Mo(VI) valencies are trapped in specific cation sites whereas at other sites considerable Mo(V)–Mo(VI) mixing occurs; Mo(IV) contributions are ruled out. The class II mixed valence system $TeMo_5O_{16}$ is formally best described as TeO_2·$3MoO_3$·Mo_2O_5. Assignments of skeletal modes are suggested for MoO_3, α-MoO_3·H_2O, α-Te_2MoO_7 and $TeMo_5O_{16}$.

Introduction

Recent interest in the binary system (Te, Mo)O originates from the application of these mixed oxides as catalysts in the (amm) oxidation of olefins with selectivities easily exceeding 90% [1–7]. The superior activity of the system as compared to other TeO_2-based binary systems [8] has led to many efforts to investigate the solid state and structural properties of the system. Two new phases, Te_2MoO_7 (in the crystalline α and glassy β form) and $TeMo_5O_{16}$, have been identified and detailed information about their morphology, bonding properties, stereogeometries and the type of network formed by the co-ordination polyhedra is now available [9–15]. The final aim of these studies is to arrive at a correlation of the catalytic activity and selectivity of these oxides with their chemical and physical properties. It is obvious that a spectroscopical characterization of the system can make a useful contribution to the elucidation of the problem.

In this paper we report the results of investigations by means of X-ray photoelectron spectroscopy (XPS) and infrared and Raman vibrational spectroscopy of the compounds Te_2MoO_7 and $TeMo_5O_{16}$, the crystal structures of which have recently been determined [13–15]. This permits a comparison of the bonding situations of the atoms in these mixed oxides.

Experimental

Materials

α-Te_2MoO_7 was an original sample from ref. [9]. $TeMo_5O_{16}$ was prepared according to ref. [10]. α-MoO_3·H_2O was kindly supplied by Prof. B. Krebs. α-TeO_2 and MoO_3 were commercial (Schuchardt and C. Erba) analytical-grade products.

Spectroscopic Techniques

XPS spectra were recorded with an AEI ES 200B instrument using the MgKα_{12} line (1253.7 eV) for excitation. The X-ray power supply was run at 15 kV and 20 mA. Samples were in the form of powder dispersed on double-sided insulating tape ('Scotch' brand). In order to compensate for the effects of sample charging spectra were referenced to the C(1s) line (core-electron binding energy E_b = 284.8 eV) attributable to hydrocarbon contamination. Deconvolution of 'mixed' spectra has been performed with a Du Pont 310 Curve Resolver requiring that (*a*) the deconvoluted spectra of Gaussian shape sum to the total (experimental) manifold; (*b*) the peak splitting Mo($3d_{3/2}$) – Mo($3d_{5/2}$) = 3.0 eV ± 0.1 eV; (*c*) the ratio Mo($3d_{5/2}$)/Mo($3d_{3/2}$) = 6/4; (*d*) the final binding energies of the principal constituents be essentially constant.

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TABLE I. Experimental Binding Energies.

Compound	Te(3d$_{5/2}$)	Mo(3d$_{5/2}$)	Mo(3p$_{3/2}$)	O(1s)
$TeMo_5O_{16}$	577.9	232.5^a 233.1	399.3	532.0 532.8^a
α-Te_2MoO_7	578.1	233.2	399.7	532.2 533.5^a
MoO_3	–	233.5	399.8	532.2
α-TeO_2	577.6	–	–	532.2 534.0^a

^{a}Component at lower intensity.

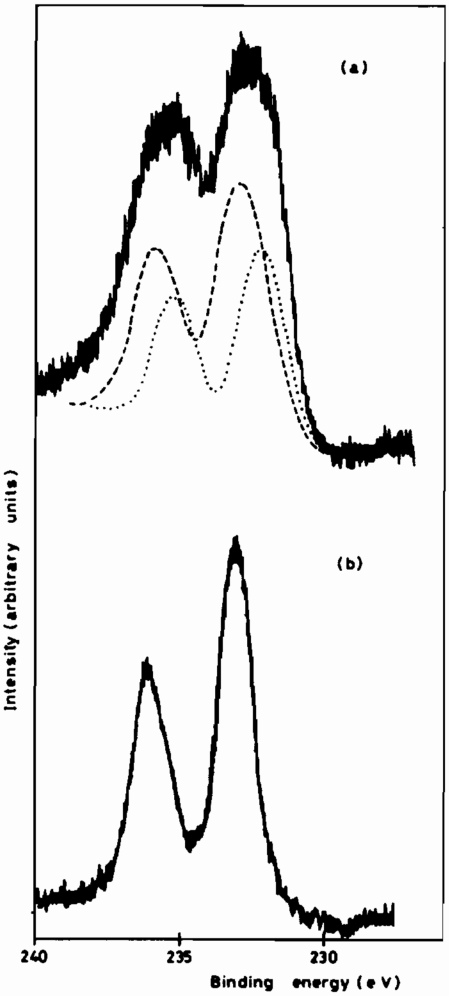

Fig. 1. Molybdenum 3d doublet XPS spectrum of $TeMo_5O_{16}$ (a) and α-Te_2MoO_7 (b).

Infrared, Raman and optical reflectance spectra were taken with a Perkin-Elmer model 621, Coderg PHO and Beckman Acta MIV spectrophotometer, respectively, using the KBr technique in the former case.

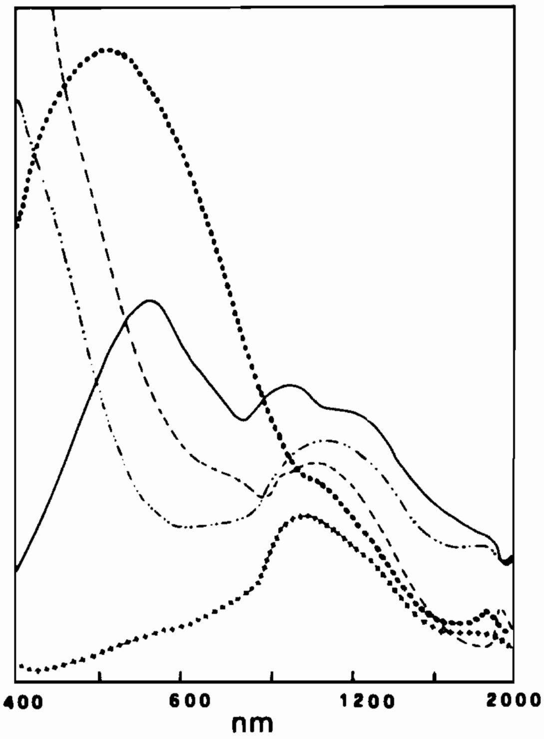

Fig. 2. Diffuse reflectance spectra of $TeMo_5O_{16}$ (———), α-Te_2MoO_7 (– – – –), TeO_2 (–··–), MoO_2 (oooo) and MoO_3 (*****).

Results

Table I compares the results of XPS measurements of the mixed oxides with those of MoO_3 and TeO_2. Only the high intensity component of the doublets corresponding to the 3d and 3p levels is reported as the energy gap between the two components was constant in the compounds investigated and independent of oxidation state, namely E(Mo3d$_{3/2}$) – E(Mo3d$_{5/2}$) = 3.0 eV, E(Mo3p$_{1/2}$) – E(Mo3p$_{3/2}$) = 17.4 eV, E(Te3d$_{3/2}$) – E(Te3d$_{5/2}$) = 10.4 eV; the areas of the bands of the multiplet were found to be in the correct statistical ratio of 3:2 and 2:1, as required for the components of the 3d and 3p levels, respectively. Figure 1 shows the Mo(3d) level as observed in α-Te_2MoO_7 and $TeMo_5O_{16}$, together with the deconvolution in the latter case. The presence of two non-equivalent molybdenum bonding types in $TeMo_5O_{16}$ is responsible for the increase in linewidth as compared to α-Te_2MoO_7 and points to mixed valency effects. The observed downfield shift in binding energy experienced by one of the contributors to the Mo(3d) spectra indicates reduced Mo-species. Observations similar to those for the Mo(3d)

TABLE II. Bond Valence Sums and Stereogeometries in Mixed-valency Oxotellurium Compounds.

Compound	$\Sigma s_{\mathrm{Te(VI)-O}}$ (v.u.)[a,b]	$\Sigma s_{\mathrm{Te(IV)-O}}$ (v.u.)[a,b]	Coordination type		Ref.
			Te(VI)	Te(IV)	
Te_2O_5	5.88(2)	3.82(2)	Oct.[c]	[2 + 2]	d
Te_4O_9	5.71(9)	3.83(3)	Oct.	[3 + 1]	e
$H_2Te_2O_6$	5.89(2)	3.95(2)	Oct.	[2 + 2]	f
$K_2Te_4O_{12}$	6.00(5)	3.93(2)	Oct.	[3 + 2][g]	h
	6.14(8)		Oct.		
	5.92(4)		Oct.		
	5.57(10)		[4 + 2][i]		

[a] Bond valence equations: $s = (d/1.911)^{-7.0}$ for Te(VI) and $s = (d/1.933)^{-4.5}$ for Te(IV) (ref. [20]). [b] σ_s has been calculated for the shortest $d_{\mathrm{Te-O}}$. [c] Oct. indicates a fairly regular octahedron. [d] O. Lindqvist and J. Moret, *Acta Cryst.*, *B29*, 643 (1973). [e] O. Lindqvist, W. Mark and J. Moret, *Acta Cryst.*, *B31*, 1255 (1975). [f] O. Lindqvist and J. Moret, *Acta Cryst.*, *B29*, 956 (1973). [g] Exceptional case of TeO_5E environment. [h] F. Daniel, J. Moret, M. Maurin and E. Philippot, *Acta Cryst.*, *B34*, 1782 (1978). [i] Highly distorted octahedron.

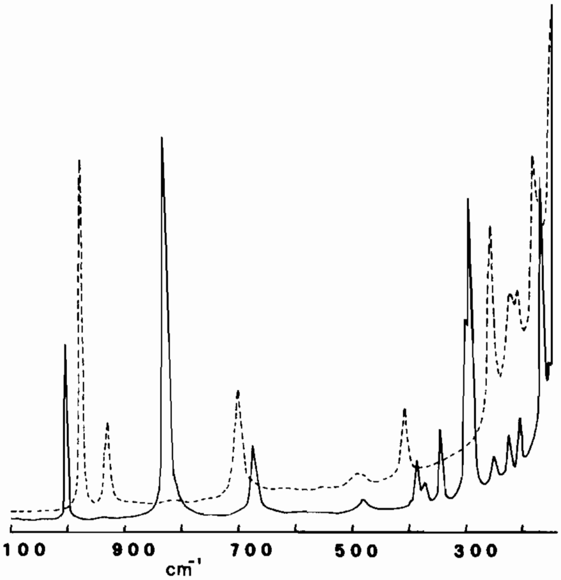

Fig. 3. Raman spectra on solid samples of MoO_3 (———) and α-$MoO_3 \cdot H_2O$ (– – –).

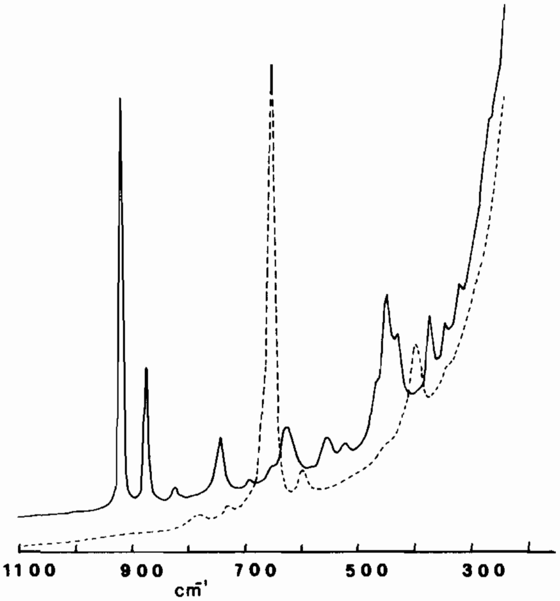

Fig. 4. Raman spectra on solid samples of α-Te_2MoO_7 (———) and TeO_2 (– – –).

level were made for the energy variations of the Mo(3p) level (Table I). However, due to its inherently higher band width, this core level is less suitable than Mo(3d) in revealing fine structure details. Consequently deconvolution of the 3p band and resolution of the two components associated with the different molybdenum cations in $TeMo_5O_{16}$ is more difficult. The O(1s) band of all four compounds is found at about 532 eV with a minor component at higher energies, except for MoO_3.

Diffuse reflectance spectra of α-Te_2MoO_7, $TeMo_5O_{16}$, MoO_3, MoO_2 and TeO_2 in the range 400–2000 nm are shown in Fig. 2. The infrared and Raman spectra of MoO_3, α-$MoO_3 \cdot H_2O$, α-TeO_2, α-Te_2MoO_7 and the IR spectrum of $TeMo_5O_{16}$ are reported in Figs. 3–6.

Discussion

It has recently been found that α-Te_2MoO_7 presents a [2 + 2] oxotellurium environment, just as α-TeO_2, together with a fairly similar [3 + 1] coordination [13]. These stereochemical aspects favour a valence structure Te_2(IV)Mo(VI)O_7 as Te(VI) always exhibits a characteristic octahedral oxotellurium polyhedron with a much reduced tendency for unusual stereochemistry. This is confirmed by structural data for mixed valency structures of tellurium (Table II) and rules out a description of Te_2MoO_7 as Te(IV)Te(VI)Mo(IV)O_7 and actually settles the question of valence isomerism of the

TABLE III. Structural Data of Tellurium–Molybdenum Oxides.

Compound	Cation (M)[a]	Σs_{M-O} (v.u.)[b,c]	Coordination Type[d]	Ref.
MoO_3	Mo	5.92(6)	[2 + 2 + 2]	f
α-Te_2MoO_7	Mo	5.75(4)	[2 + 2 + 2]	g
	Te(1)	4.04(3)	[3 + 1]	
	Te(2)	4.02(3)	[2 + 2]	
$TeMo_5O_{16}$	Mo(1)	5.97(6)	[3 + 3]	h
	Mo(2)	5.65(6)	[1 + 2 + 2 + 1]	
	Mo(3)	5.57(6)	[1 + 2 + 2 + 1]	
	Mo(4)	5.44(6)	[1 + 2 + 2 + 1]	
	Mo(5)	5.65(6)	[1 + 2 + 2 + 1]	
	Te	[3.44(4)][e]	[3 + 1]	
α-TeO_2	Te	3.91(10)	[2 + 2]	i

[a] Cation numbering scheme in accordance with the original papers. [b] Bond valence equations: $s_{Mo-O} = (d_{Mo-O}/1.882)^{-6.0}$ and $s_{Te-O} = (d_{Te-O}/1.933)^{-4}$. (ref. [20]). [c] σ_s has been calculated for the shortest d_{M-O}. [d] *Cf.* ref. 13. [e] Contributions of primary bonds only. *Cf.* note *d* of Table IV. [f] L. Kihlborg, *Arkiv Kemi, 21*, 357 (1963). [g] Ref. 13. [h] Ref. 15. [i] O. Lindqvist, *Acta Chem. Scand., 22*, 977 (1968).

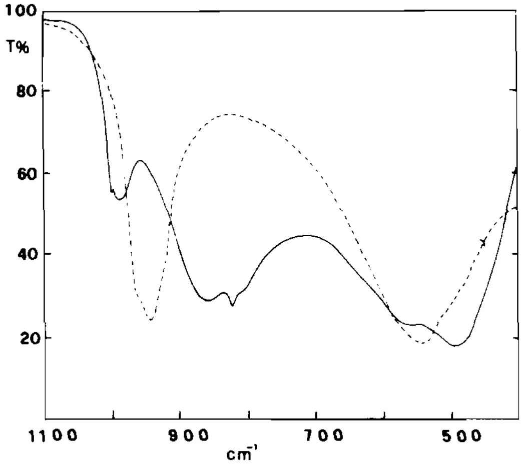

Fig. 5. Infrared spectra in KBr pellets of MoO_3 (——) and α-$MoO_3 \cdot H_2O$ (– – –).

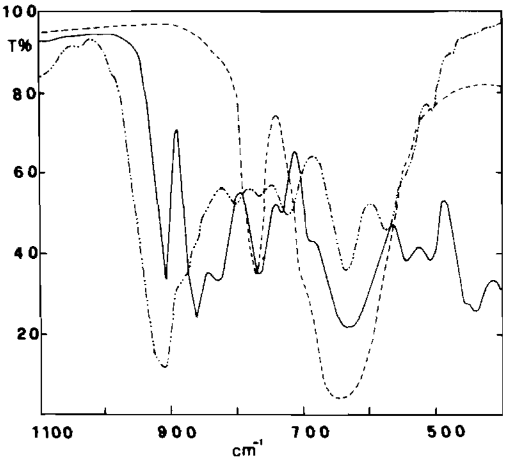

Fig. 6. Infrared spectra in KBr pellets of α-Te_2MoO_7 (——), TeO_2 (– – –) and $TeMo_5O_{16}$ (–··–).

compound. Similarly, $TeMo_5O_{16}$ may be formulated either as Te(VI)Mo_2(IV)Mo_3(VI)O_{16} or as Te(IV)Mo(IV)Mo_4(VI)O_{16} (if we consider only Mo(IV) and (VI) valent states); also in this case the crystal structure determination [15] qualitatively indicates the absence of Te(VI) on the same grounds as above, thus favouring the Te(IV) isomer. Our conclusions are confirmed quantitatively by the use of the bond-strength(s) bond-length(d) relationship $s_{Te-O} = (d_{Te-O}/1.933)^{-4.5}$, as shown in Table III.

The results obtained by XPS for α-TeO_2, α-Te_2MoO_7 and $TeMo_5O_{16}$ are in accordance with the structural data described above. As the small stereogeometric differences in the oxotellurium polyhedra are unlikely to influence appreciably the charge distribution on the cations, essentially equal Te(3d) binding energies are expected in the three compounds, as is indeed observed.

With regard to molybdenum, we notice that the charge potential model [16] permits to establish a relationship between the charge distribution of an atom and the observed chemical shifts of the core levels. In this approach to rationalize variations in binding energy the assumption is made that the contribution of the Madelung type intramolecular potential of the other atoms present is roughly of the same order of magnitude in the compounds under consideration. Therefore, only in a series of related compounds shifts of specific core levels qualitatively reflect differences in the charge distribution. The Mo($3d_{5/2}$) binding energy of α-Te_2MoO_7 (233.2 eV) and of some of the cations in $TeMo_5O_{16}$ (233.1 eV) is only slightly lower than that observed in MoO_3 (233.5 eV). This is interpreted as evidence in favour of the Mo(VI) valent state. The observed second component of the Mo($3d_{5/2}$) bond energy at 232.5

eV in $TeMo_5O_{16}$ indicates molybdenum atoms carrying a less positive charge. If we take the linear correlation of E and oxidation number according to Haber *et al.* [17], which differs from considerations of Cimino and De Angelis [18], it appears that the observed $\Delta E = -0.6$ eV (referred to the Mo(VI) band position in $TeMo_5O_{16}$) is best interpreted as corresponding roughly to a unitary oxidation change and thus suggests Mo(V) cation contributions. This permits a formal description of the compound as $Te(IV)Mo_2(V)Mo_3(VI)O_{16}$. The intensity ratio (approximately 1.5) between the Mo(3d) components at higher and lower binding energy also supports the formula $TeO_2 \cdot 3MoO_3 \cdot Mo_2O_5$.

It has recently been argued that appearance of two peaks for an inner-shell transition does not prove the existence of a trapped-valence ground state [19]. This is because of possible relaxation processes of the valence-electron during photoionization. However, in the present case the existence of distinct Mo(V) and Mo(VI) centres, albeit with a large amount of mixing, finds other independent support. Namely, the distribution of the Mo valence population over the available cation sites can be derived from a detailed consideration of the Mo–O bond strengths in $TeMo_5O_{16}$ according to the relation $s_{Mo-O} = (d_{Mo-O}/1.882)^{-6.0}$ (valid for Mo(II) to Mo(VI) [20, 21]). Table III shows that apparently only in the cation site with a [3 + 3] oxo-configuration a Mo(VI) valency is trapped as opposed to extensive electron delocalization or a statistical distribution of Mo(V) and Mo(VI) cations at the other, essentially [1 + 2 + 2 + 1], oxomolybdenum sites.

Table I suggests that various types of lattice oxygen are present in the tellurium containing oxide but not in MoO_3; this is in accordance with data reported for H_2-reduced MoO_3 [17]. Detailed examination of the oxygen bonding scheme, reported in Table IV for α-Te_2MoO_7 and $TeMo_5O_{16}$, does not offer a clue to interpret the data. Moreover, a distinction between oxygens according to their cation bonding characteristics (terminal or bridging; bonded to Mo and/or Te) also fails to explain the observations and anyway, such features are not expected to lead to substantial shifts in binding energies. Probably other phenomena, such as adsorbed oxygen species, are therefore responsible for the minor O(1s) side band at higher energies in α-TeO_2, α-Te_2MoO_7 and $TeMo_5O_{16}$.

The results reported here, namely the presence of metal ions in $TeMo_5O_{16}$ in ligand fields of nearly identical symmetry, differing from one another by distortions up to a few tenths Å, with valencies distinguishable but with considerable delocalization, are characteristic of a class II mixed valence system in Robin and Day's classification scheme [22]. We then expect a mixed valence transition in the visible region (14,000–27,000 cm^{-1}), as indeed observed for $TeMo_5O_{16}$ at 550 nm (Fig. 2), which is absent in the spectra of the constituent oxides taken separately. This position of the band is similar to that of the 500 nm d–d transition of MoO_2. It is also in accordance with that calculated from the relation between frequency of the first d–d transition band and number of d–electrons per cation, as proposed by Porter *et al.* [23], namely 560 nm for a mean oxidation state of molybdenum of 5.6, which confirms our previous deductions. As expected, α-Te_2MoO_7 does

TABLE IV. Oxygen Bond Valence Sums (v.u.) in α-Te_2MoO_7 and $TeMo_5O_{16}$.[a]

α-Te_2MoO_7

Atom	Σs_{Mo-O}	Σs_{Te-O}[b]	Σs_{Te-O}[c]	Σs
O(1)	1.72		0.28	2.00
O(2)	1.86			1.86
O(3)	1.31	0.52		1.83
O(4)	0.87	1.11		1.98
O(5)		1.80	0.26	2.06
O(6)		1.94	0.23	2.17
O(7)		1.92		1.92

$TeMo_5O_{16}$[d]

Atom	Σs_{Mo-O}	Σs_{Te-O}[e]	Σs_{Te-O}[f]	Σs_{Te-O}[g]
O(1)	1.09	0.82	1.34	
O(2)	1.01	0.94	0.56	
O(3)	0.49	1.34	1.29	
O(4)	1.49	0.34		0.19
O(5)	2.01			
O(6)	2.13			
O(7)	2.07			
O(8)	1.90			0.18
O(9)	2.14			
O(10)	1.97			
O(11)	2.01			
O(12)	1.99			
O(13)	2.00			
O(14)	1.80			0.29
O(15)	2.12			
O(16)	2.07			

[a] Bond valence equations as in Table III. [b] Contributions of primary bonds. [c] Contributions of secondary bonds. [d] Calculated Te–O distances, based on published positional parameters, differ from those reported in ref. 15 and suggest a tetrahedral TeO_3E unit (σ configuration) rather than the reported [3 + 1] or β Te(IV) configuration. From the calculated sum of the Te–O bond orders (3.85 v.u. on the basis of the reported positional parameters, 3.44 v.u. with reference to published *primary* bond lengths) it is not possible to make a choice between the two alternatives. However, data reported in this table favours the originally reported bond distances, and thus merely suggests a misprint in the published Te coordinates. [e] Calculated on the basis of reported bond lengths [15]. [f] Calculated for primary bonds using published positional parameters. [g] Calculated for secondary bonds using published positional parameters.

TABLE V. Infrared and Raman Mo–O stretching frequencies.[a - c]

MoO_3				α-$MoO_3 \cdot H_2O$			
Mo–O (A)	B.O. (v.u.)	ν (cm^{-1})		Mo–O (A)	B.O. (v.u.)	ν (cm^{-1})	
		R	IR			R	IR
1.671	2.04	998(14)	1000sh	1.687	1.93	973(100)	963sh
		–	986m	1.688	1.92	927(18)	942s
1.734	1.64	–	860s	1.949	0.81	696(23)	545s
		822 (100)	820w	1.959	0.79		
1.948	0.81	668(8)	565sh	2.277	0.32	480(0.8)	–
1.948	0.81			2.346	0.27	410(12)	–
2.251	0.34	474(1.1)	490s				
2.332	0.28	370(3.5)	–				

α-Te_2MoO_7				$TeMo_5O_{16}$					
Mo–O (A)	B.O. (v.u.)	ν (cm^{-1})		Mo–O (A)	B.O. (v.u.)	ν (cm^{-1}) IR	⟨Mo–O (A)⟩	B.O. (v.u.)	ν (cm^{-1}) IR
		R	IR						
1.720	1.72	913(100)	908s	1.691	1.90	913vs	1.698	1.85	913vs
1.723	1.72	871(25)	862s	1.783	1.38	800w	1.876	1.02	d
1.928	0.86	741(18)	732sh	1.806	1.28	725m	1.881	1.00	d
1.940	0.83	550(10)	550m	2.121	0.49	540sh	1.946	0.82	d
2.132	0.47	520(3.5)	510m	2.136	0.47		2.205	0.64	575m
2.534	0.17	–	–	2.149	0.45	500w	2.409	0.23	–

[a] Structural data from references in Table VI. [b] Mo–O bond valence equation as in Table III. [c] w = weak, m = medium, s = strong, v = very, sh = shoulder. [d] Obscured by the 630 cm^{-1} band (Te–O stretching mode).

not exhibit a d–d transition. It may also be seen from Fig. 2 that both binary compounds, α-Te_2MoO_7 and $TeMo_5O_{16}$, present the spectra of the constituent oxides at very nearly their normal frequencies.

Infrared and Raman Spectra

In spite of their great industrial interest few attempts have been made so far to assign Mo–O stretching modes to molybdates and molybdenum containing mixed oxides. This is not surprising as molybdenum belongs to a select group of cations with highly distorted cation environment [24]. As a consequence, our current knowledge is practically confined to the general observation that strong absorption in the 820–840 cm^{-1} and 800–1000 cm^{-1} region are characteristic of MoO_4^{2-} tetrahedral and MoO_6^{6-} octahedral coordination, respectively [25]. The great variety in oxomolybdenum coordinations with an almost continuous spectrum of stereogeometries implies that the more fundamental individual bond-strengths are likely to be more helpful for assignment purposes than classifications in terms of group frequencies. Recent work on bond-strength bond-length relationships provides the necessary link to the available structural data. Even then it is still extremely difficult to make a complete assignment of the observed spectral bands owing to the complex nature of the metal-oxygen linkages and the distortions present in the metal–oxygen polyhedra.

Following up claims in the literature relating catalytic performance in oxidation reactions of hydrocarbons to certain spectral features of molybdates [26] we have started systematic work to index the infrared and Raman spectra. In this paper we report vibrational data (Figs. 3–6) for α-Te_2MoO_7 and $TeMo_5O_{16}$ on the basis of their crystal structures and analyze the results by comparison with MoO_3 and α-$MoO_3 \cdot H_2O$.

Comparison of Figs. 3 and 4 shows that the general features of the Raman spectrum of α-Te_2MoO_7 more closely resemble α-$MoO_3 \cdot H_2O$ than MoO_3. It is our view that this depends upon the fact that the Mo–O bond strength variations between stronger Mo–O links in MoO_3 are greater than those of α-$MoO_3 \cdot H_2O$ and α-Te_2MoO_7 (*cf.* Table V).

With regard to assignment of Mo–O stretching modes, in Table V, we have listed bond order values for the various MoO_6-units as calculated according to Brown and Wu [20]. On the basis of the calculated bond strength distribution and criteria used previously for similar compounds [27, 28], we consider the stretching modes of Mo–O bonds with greatly different bond strengths to be completely independent. We therefore assume that vibrational

TABLE VI. Site Symmetry of MoO Units.

Compound	Factor group	Z[a]	Site symmetry	Ref.
MoO_3	$Pbnm \equiv D_{2h}^{16}$	4	C_s	b
α-$MoO_3 \cdot H_2O$	$P\bar{1} \equiv C_i^1$	2	C_1	c
α-Te_2MoO_7	$P2_1/c \equiv C_{2h}^5$	4	C_1	d
$TeMo_5O_{16}$	$P2_1/c \equiv C_{2h}^5$	4	C_1	e

[a] Number of molecules per unit-cell. [b] L. Kihlborg, *Arkiv Kemi, 21,* 357 (1963). [c] I. Böschen and B. Krebs, *Acta Cryst., B30,* 1795 (1974). [d] Ref. [13]. [e] Ref. [15].

coupling occurs only for stretching modes of Mo–O bonds of similar bond strength. In the assignment of the vibrational bands it should be considered that for the compounds investigated, which crystallize in centric space-groups with $Z > 1$ (Table VI), each fundamental vibration of the MoO_6 moiety may give an active Raman and IR vibration due to vibrational coupling between different molecules.

The resulting assignments of the absorption frequencies, reported in Table V, have been obtained by first considering the Raman and IR vibrational bands of MoO_3, α-$MoO_3 \cdot H_2O$ and α-Te_2MoO_7 corresponding to the shortest Mo–O bond. Because of the low site symmetry of the MoO_6-units (Table VI) at least one Raman and one IR band were taken for each compound. In case of MoO_3, where one strongly bonded terminal oxygen is somewhat less remote than another atom partaking in continuous Mo–O–Mo chains, the highest Raman and IR frequencies have been chosen. The non-coincidence of the two frequencies may depend upon the vibrational coupling between the molecules in the unit-cell. In cases such as α-$MoO_3 \cdot H_2O$ and α-Te_2MoO_7, where the MoO_6-unit contains two strong Mo–O bonds of equal bond order (b.o.) at least two IR and two Raman bands, within a small spectral range, were assigned to the Mo–O stretching modes of these bonds. We notice that the absorption bands taken into account so far relate to Mo–O bonds with b.o. > 1.5 v.u. and further that the frequency values assigned all lie above about 830 cm^{-1}, *i.e.* above the range usually assigned to the group frequencies of regular MoO_4^{2-}-tetrahedra (b.o. = 1.5 v.u.).

For the assignment of the frequencies characteristic of bonds with b.o. ≈0.8 v.u., present in all compounds examined, internal force constants were calculated from the average values of the previously assigned Raman and IR frequencies for stretching modes of bonds of b.o. >1.5 v.u. These force constant values vary linearly with bond order, in analogy to the findings of Cotton and Wing [29], even though calculation of the constant of interaction between the Mo–O stretchings was neglected and mean frequencies were taken. The resulting diagram (Fig. 7) can then be used to derive mean frequencies for the weaker bonds and Raman and IR absorption bands were assigned, again within a small spectral range, to stretchings of Mo–O bonds with b.o. ≈0.8 v.u. Our assignment for MoO_3 differs from that of Barraclough *et al.* [30] who attributed the 860 and 820 cm^{-1} bands to stretching vibrations due to two *distinct* continuous Mo–O–Mo structures. Instead, we ascribe the 565 cm^{-1} band to the one Mo–O–Mo chain with Mo–O bond lengths of 1.948 Å. Although similar criteria as above were used in the assignment of the frequencies of the weakest bonds (b.o. <0.8 v.u.) considerably more uncertainties were encountered here due to the presence of the δ (O–Mo–O) deformations in the same spectral range [31, 32].

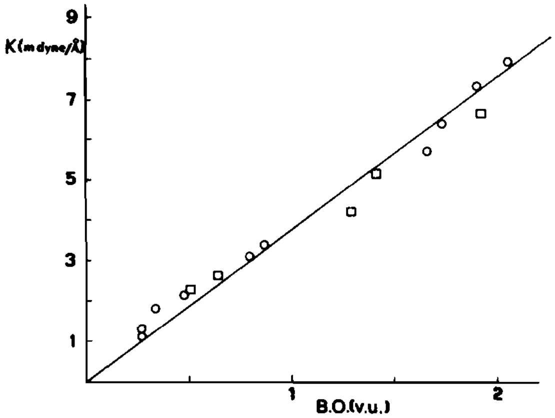

Fig. 7. Internal force constants of Mo–O stretching vibrations as a function of Mo–O bond order. *Cf.* Table V for numerical values of MoO_3, α-$MoO_3 \cdot H_2O$ and α-Te_2MoO_7 (○) and $TeMo_5O_{16}$ (□).

It is of interest to notice that the $\nu_{as}(Mo_2O)$ frequency corresponding to the one almost linear oxygen bridge in α-Te_2MoO_7 (IR, 862 cm^{-1}) is close to the value of 860 cm^{-1} expected by Griffith *et al.* [33]. The assignment for the other Mo–O–M bridge vibration, 732 cm^{-1} (IR), is in accordance with the bent-bridge normal vibrations according to Jeżowska-Trzebiatowska [34]. The stretching modes associated with the two-oxygen bridge Mo_2O_2 in α-Te_2MoO_7 are found at 510 and 550 cm^{-1} (IR) and at 520 and 550 cm^{-1} (R), again in the range expected by Griffith *et al.* [35]. The absorption bands at 830 cm^{-1} (IR) and 821 cm^{-1} (R) in the α-Te_2MoO_7 spectra may be combination bands or harmonics or due to stretching vibrations of Mo–O bonds with b.o. = 1.72 v.u. (in the latter case the factor group thus induces three IR and Raman active bands for these stretching vibrations). It is not surprising to find that the assignments of Table V for MoO_3 and α-Te_2MoO_7 differ from those of Arnaud *et al.* [7], as the latter are based on a less accurate treatment of experimental data. Consequently, conclusions contained in ref. [7] concerning the most weakly bonded oxygens and their bearings upon catalysis, seem valueless.

Although MoO_3, α-$MoO_3 \cdot H_2O$ and α-Te_2MoO_7 can all be considered to contain *cis*-dioxo units, it is clear from the reported Mo-O bond strengths in Table V that the frequencies vary considerably from those indicated for *cis*-dioxo complexes with doubly bonded oxygens, namely near 950 and 900 cm^{-1} [36]; however, this is quite understandable in view of the almost continuous nature of oxomolybdenum configurations [13].

Assignment of vibrational frequencies to $TeMo_5O_{16}$ has been more complicated as the intense black-violet colour of the compound has prevented us from recording Raman data and also because of the complex crystal structure consisting of one [3 + 3] type MoO_6-unit and four [1 + 2 + 2 + 1] octahedra, all with rather different values of Mo–O bond orders. Assignments of Table V are based on the averaged dimensions of the [1 + 2 + 2 + 1] octahedra and on the values of the force constants according to Fig. 7. In this figure we have subsequently reported the calculated force constants following from the assignments of Table V. The fairly substantial deviations from linearity for $TeMo_5O_{16}$ may depend upon the scarcity of experimental data in the absence of the Raman spectrum. Yet, the findings for $TeMo_5O_{16}$, namely considerably lower stretching frequencies for the strongest bonds than in molybdenyl-containing compounds are in line with other 1,2,3 trioxo-complexes [36].

As a result of our analysis, the observed frequencies (cm^{-1}) at 765m, 960sh, 630s (IR, α-Te_2MoO_7), 620m (R, α-Te_2MoO_7) and 765 w, 630m (IR, $TeMo_5O_{16}$) should be ascribed to Te–O vibrational modes. This is in reasonable accordance with the α-TeO_2 spectral data, namely at (cm^{-1}) 784 vw, 649s, 592w(R) [37], and 760m, 714vs, 648vs (IR) [38], where the postscripts have the same meaning as in Table V.

Acknowledgements

Thanks are due to Prof. B. Krebs (Bielefeld) for kindly supplying the original sample of α-$MoO_3 \cdot H_2O$ and to Dr. D. T. Clark (Durham) for useful discussions.

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