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The characteristic IR spectra of heterothiometallic cluster compounds

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Abstract

This article summarizes and presents the obtainable characteristic IR spectra of the existing heterothiometallic cluster compounds containing the $[MXS_3]^{2-}$ (X = O, S; M = V, Mo, W, Re) moiety. The M–S stretching vibration modes are classified into four categories including ν(M–S_t), ν(M–μ_2-S), ν(M–μ_3-S) and ν(M–μ_4-S) according to the different conjunction ways between the transition metal and sulfur atoms. The structures of the heterothiometallic cluster compounds could be inferred from their characteristic IR spectra, the core structure's symmetry of the heterothiometallic clusters and the M/M′ ratio.

Keywords: Characteristic IR spectra; Heterothiometallic cluster compounds

1. Introduction

Heterothiometallic cluster chemistry is one of the most important and active areas in inorganic and physical chemistry [1–6] because it plays a special role in catalysis reactions [7–10], biological processes [11–13] and advanced materials [14–16]. During the past two decades, over 300 heterothiometallic cluster compounds containing the $[MXS_3]^{2-}$ (X = O, S; M = V, Mo, W, Re) moiety have been synthesized and studied extensively [17–19]. However, the IR spectra of the heterothiometallic clusters have not been studied and summarized systematically. The relationship between the IR spectra of the heterothiometallic clusters and their structures has not been investigated thoroughly. The IR spectra of heterothiometallic cluster compounds as well as their UV–vis spectra, Elemental analyses and Raman spectra are usually regarded as supplemental proofs of the crystal structures determined by X-ray diffraction. In this article, the characteristic IR spectra of the heterothiometallic clusters with the $[MXS_3]^{2-}$ moiety are studied and summarized systematically. The structures of the heterothiometallic clusters could be inferred by studying and analyzing their characteristic IR spectra, the core structure's symmetry, and the M/M′ ratio.

2. General study

The low wave-number region of the IR spectra of heterothiometallic cluster compounds containing the $[MXS_3]^{2-}$ (X = O, S; M = V, Mo, W, Re) moiety has proven valuable in arguments concerning their electronic and structural characteristics [1b,17,19]. The $[MXS_3]^{2-}$ moiety as a bidentate ligand always coordinates with M′ (M′ = Cu, Ag, Au, Pd, Pt, Zn, Cd, Hg, Fe, Co, Ni, Sn, Ru) in the pattern of  , while according to our knowledge, only one example (Table 1, no. 95) with another conjunct pattern M–S–M′, has been found.

The molecular spherical space arrangement of every heterothiometallic cluster compound containing the $[MXS_3]^{2-}$ moiety may be divided into three spheres. There are four or three sulfur atoms and one oxygen atom in the first sphere. The

Table 1
IR spectral parameters of the first category of the heterothiometallic cluster compounds

Number	Compound	M–S_t	M–μ_2-S	M–μ_3-S	M–μ_4-S	M-μ_c-S	Symmetry group of core	Ref.
1	$[NH_4]_2[MoS_4]$	480					T_d	[23]
2	$[Et_4N]_2[MoS_4]$	470					T_d	[23]
3	$[AgMoS_4{\cdot}2\text{-}MePyH]_n$		439				C_{2v}	[24]
4	$[AgMoS_4{\cdot}4\text{-}MePyH]_n$		445				C_{2v}	[24]
5	$[PPh_4]_2[(CuCN)MoS_4]$	500, 486	447				C_{2v}	[30]
6	$[PPh_4]_2[(CuNCS)MoS_4]$	495, 485	450, 440				C_{2v}	[18]
7	$[PPh_4]_2[(PhSCu)MoS_4]$	491, 479	440				C_{2v}	[18]
8	$[(phen)_2Cu_2MoS_4]$		460				D_{2d}	[18]
9	$[PPh_4]_2[(CuNCS)_2MoS_4]$		467				D_{2d}	[31]
10	$[PPh_4]_2[(PhSCu)_2MoS_4]$		470, 462				D_{2d}	[18]
11	$[Et_4N]_2[(CuCN)_2MoS_4]{\cdot}H_2O$		475				D_{2d}	[32]
12	$[(PPh_3)_3Cu_2MoS_4]{\cdot}0.8CH_2Cl_2$		465				D_{2d}	[18]
13	$[(PPh_3)_3Ag_2MoS_4]{\cdot}0.8CH_2Cl_2$		467, 458				D_{2d}	[34]
14	$[Et_4N]_2[MoS_4(CuS_2CNMe_2)_2]$		450				D_{2d}	[33]
15	$[Et_4N]_2[MoS_4(CuS_2CNEt_2)_2]$		463				D_{2d}	[21]
16	$[MoCu_2S_4(dppe)_2]$		465				D_{2d}	[21]
17	$[MoS_4Au_2(AsPh_3)_2]$		453.4				D_{2d}	[35]
18	$[(PPh_3)_3Cu_3ClMoS_4]$	527, 515		447, 441			C_{3v}	[34]
19	$[(PPh_3)_3Cu_3BrMoS_4]$	491.4, 487		453			C_{3v}	[39]
20	$[(PPh_3)_3Cu_3IMoS_4]$	490		466			C_{3v}	[39]
21	$[(Ph_3As)_3Cu_3IMoS_4]$	527		443			C_{3v}	[40]
22	$[(PPh_3)_3Ag_3IMoS_4]$	516		433			C_{3v}	[41]
23	$[MoS_4Ag_3(PPh_3)_3(S_2P(OBu)_2)]$	495		439.2		418.2	C_{3v}	[42]
24	$[Bu_4N]_3[MoS_4Ag_3BrI_3]$	488		426.8			C_{3v}	[43]
25	$[Et_4N]_2[MoCu_3S_4(S_2CNEt_2)_3]$		463	436			C_{2v}	[21]
26	$[Et_4N]_2[MoCu_3S_4(S_2CNC_5H_{10})_3]$		463	442			C_{2v}	[44]
27	$[Et_4N]_4[I_6Cu_4MoS_4]$			442			D_{4h}	[45]
28	$[Ph_4P]_2[(CuNCS)_4MoS_4]$			454			D_{4h}	[31]
29	$[Et_4N]_2[(CuNCS)_4MoS_4]$			458, 447			D_{4h}	[31]
30	$[Et_4N]_3[Cu_4(NCS)_5MoS_4]$			456			D_{4h}	[31]
31	$[(4\text{-}MePy)_4(NCS)_2Cu_4MoS_4]$			450			D_{4h}	[18]
32	$[Py_6(SCN)_2Cu_4MoS_4]$			447			D_{4h}	[46]

Table 1 (*Continued*)

Number	Compound	M–S_t	M–μ_2-S	M–μ_3-S	M–μ_4-S	M-μ_c-S	Symmetry group of core	Ref.
33	$[MoS_4Cu_4(4\text{-}MePy)_8][Mo_6O_{19}]$			439.2			D_{4h}	[47]
34	$[MoCu_4S_4Cl_2Py_6]$			447		415	D_{4h}	[48]
35	$[Bu_4N]_2[MoS_4(CuCl)_4]$			460			D_{4h}	[49]
36	$[PPh_4]_2[MoS_4(CuBr)_4]\cdot Me_2CO$			472, 458			D_{4h}	[50]
37	$[Et_4N]_2[MoS_4(CuCl)_5Cl_2]$			460, 448	428		C_{2v}	[52]
38	$[Me_4N]_4[MoS_4(CuCl)_5Cl_2]$			460, 448	425		C_{2v}	[52]
39	$[MoCu_6S_4Br_4Py_4]$				438		T_d	[53]
40	$[Et_4N]_4[MoS_4Cu_{10}Cl_{12}]$				434		T_d	[54]
41	$[Et_4N]_4[MoS_4Cu_{10}Br_{12}]$				425		T_d	[21]
42	$[NH_4]_2[WS_4]$	460					T_d	[23]
43	$[Et_4N]_2[WS_4]$	458					T_d	[23]
44	$[AgWS_4\cdot 2\text{-}MePyH]_n$		430				C_{2v}	[24]
45	$[AgWS_4\cdot 4\text{-}MePyH]_n$		437.3				C_{2v}	[24]
46	$[NPr_4]_2[(CuCN)WS_4]$	490, 482	450, 444				C_{2v}	[61]
47	$[WS_4AgNH_3C(CH_2OH)_3]\cdot 2DMF$	462	439.3				C_{2v}	[62]
48	$[WS_4AgNH_3C(CH_2OH)_3]\cdot H_2O$	476	445.5				C_{2v}	[62]
49	$[WS_4AgHNEt_3\cdot DMF]$	451.8	437.8				C_{2v}	[63]
50	$[(Phen)_2Cu_2WS_4]$		450				D_{2d}	[29]
51	$[PPh_4]_2[(CuNCS)_2WS_4]$		455				D_{2d}	[31]
52	$[Pr_4N]_2[(CuCN)_2WS_4]$		470				D_{2d}	[61]
53	$[PPh_4]_2[(CuCl)_2WS_4]$		460				D_{2d}	[61]
54	$[WAu_2S_4(AsPh_3)_2]$		477, 442				D_{2d}	[35]
55	$[WS_4Cu_3Cl(PPh_3)_3]$	513		436			C_{3v}	[34]
56	$[WS_4Cu_3I(AsPh_3)_3]$	515		432			C_{3v}	[40]
57	$[WS_4Cu_3Br(PPh_3)_3]$	521.5, 500.4		431			C_{3v}	[39]
58	$[WS_4Cu_3I(PPh_3)_3]$	478		448			C_{3v}	[39]
59	$[WS_4Ag_3I(AsPh_3)_3]\cdot(SAsPh_3)$	508		472			C_{3v}	[64]
60	$[WS_4Ag_3I(PPh_3)_3]\cdot H_2O$	512.5, 499		420.9			C_{3v}	[65]
61	$[Bu_4N]_3[WS_4Ag_3I_4]$	487		427			C_{3v}	[66]
62	$[WS_4Ag_3(S_2P(OEt)_2)(PPh_3)_3]$	516		445		421	C_{3v}	[67]
63	$[WS_4Ag_3Cl(PPh_3)_3]\cdot 0.5P(S)Ph_3\cdot 3H_2O$	517, 502		424			C_{3v}	[41]
64	$[PPh_4]_2[(CuCl)_3WS_4]$		460	430			C_{2v}	[68]
65	$[Et_4N]_2[(CuNCS)_3WS_4]$		471, 461	444			C_{2v}	[31]

Table 1 (*Continued*)

Number	Compound	M–S_t	M–μ_2-S	M–μ_3-S	M–μ_4-S	M-μ_c-S	Symmetry group of core	Ref.
66	$[Et_4N]_2[WS_4Cu_3(S_2CNEt_2)_3]$		450	420			C_{2v}	[69]
67	$[Et_4N]_2[WS_4Cu_3(S_2CNC_5H_{10})_3]$		455	430			C_{2v}	[44]
68	$[PPh_4]_2[(CuNCS)_4WS_4]$			433			D_{4h}	[31]
69	$[Et_4N]_2[Cu_4(NCS)_5WS_4]$			442			D_{4h}	[31]
70	$[(4\text{-}MePy)_4(NCS)_2Cu_4WS_4]$			432			D_{4h}	[18]
71	$[Py_6(SCN)_2Cu_4WS_4]$			435.2			D_{4h}	[46]
72	$[WS_4Cu_4(4\text{-}MePy)_8][W_6O_{19}]$			437.6			D_{4h}	[47]
73	$[WS_4Cu_4Cl_2Py_6]$			445		412	D_{4h}	[51]
74	$[Bu_4N]_2[WS_4Cu_4Cl_4]$			445			D_{4h}	[49]
75	$[Et_4N]_4[WS_4Cu_5Br_7]$			447	421		C_{2v}	[70]
76	$[Me_4N]_4[WS_4Cu_5Cl_7]$			450	420		C_{2v}	[52]
77	$[WS_4Cu_6Br_4Py_4]$				427		T_d	[71]
78	$[WS_4Cu_6I_4Py_4]$				430		T_d	[70]
79	$[Et_4N]_4[WS_4Cu_{10}Br_{12}]$				419		T_d	[21]
80	$[NH_4]_3[VS_4]$	478					T_d	[72]
81	$[Et_4N]_4[VFe_2S_4Cl_4]$		470, 462				D_{2d}	[72]
82	$[(PPh_3)_4Cu_3VS_4]\cdot 2CH_2Cl_2$		495	478			C_{2v}	[73]
83	$[Bu_4N]_3[VS_4(CuCN)_3]\cdot 2CH_3COCH_3$		489	473, 458			C_{2v}	[72]
84	$[Et_4N]_3[VS_4Cu_4(OC_4H_8dtc)(PhS)_3]$			464.6			D_{4h}	[74]
85	$[Et_4N]_3[VS_4Cu_4(Et_2dtc)(PhS)_3]$			462.8			D_{4h}	[74]
86	$[Et_4N]_3[VS_4Cu_4(OC_4H_8dtc)_2(PhS)_2]$			465			D_{4h}	[74]
87	$[Et_4N]_3[VS_4Cu_4(PhS)_4]$			479.4			D_{4h}	[74]
88	$[VS_4(CuPPh_3)_5Br_2]\cdot 0.5CH_2Cl_2$			458.3	437.2		C_{2v}	[75]
89	$[VS_4(CuPPh_3)_5Br_2CuX](X = 0.5Cl + 0.5Br)$				451, 442		T_d	[76]
90	$[VS_4(CuPPh_3)_5Br_2CuX]\cdot CH_2Cl_2$				451, 440		T_d	[76]
91	$[VS_4(CuPPh_3)_5(CuCl)Cl_2]\cdot CH_2Cl_2$				459, 443		T_d	[77]
92	$[VS_4Cu_6Py_8Br_3]$				444, 422		T_d	[78]
93	$[Bu_4N][ReS_4]$	484					T_d	[72]
94	$[(p\text{-}Cymene)RuClReS_4]$	524, 512	454				C_{2v}	[79]
95	$[(MeCp)Ru(dppe)ReS_4]$	490					C_{2v}	[80]
96	$[PPh_4]_2[Cl_2Fe(ReS_4)FeCl_2]$		446				D_{2d}	[81]
97	$[NPr_4]_2[ReS_4(CuCl)_3Cl]$	525		470, 439			C_{3v}	[82]
98	$[Et_4N]_2[ReS_4Cu_3I_4]$		484, 470	447, 439			C_{2v}	[83]
99	$[PPh_4]_2[ReS_4Cu_4I_5]$		488	449	421		C_1	[85]
100	$[PPh_4]_2[Et_4N][ReS_4Cu_5Cl_7]$			451	442		C_{2v}	[86]
101	$[PPh_4]_2[Et_4N][ReS_4Cu_5Br_7]$			449	440		C_{2v}	[87]
102	$[Pr_4N]_2[ReS_4Cu_5I_6]$		480	445, 438			C_{2v}	[83]

oxygen and sulfur atoms are directly connected with the transition metal atom M to form one M–O_t bond and four kinds of M–S bonds. According to the coordination number of the sulfur atom with M and M′ in  , the combination modes of S with M may be classified into four categories as follows: M–S_t, M–μ_2-S, M–μ_3-S and M–μ_4-S. The transition metal atom M can be considered as a 'nucleus' of the cluster. M′ atoms are surrounding the first sphere by conjunction between M′ and sulfur atoms. The M′–S bonds are regarded as the second sphere of the clusters in their molecular space structures. Various kinds of ligands are coordinated with the M′ atoms. This kind of coordination is thought of as the third sphere.

In this article, we will consider the effects of the molecular configurations within the first two spheres to the M–S bonds only. The diagrammatic sketch of the molecular spherical space arrangement for each heterothiometallic cluster compound containing a $[MXS_3]^{2-}$ moiety may be exhibited as follows (Fig. 1).

The four different modes of M–S_x ($x = t$, μ_2, μ_3, μ_4) result in differences in bond distances of M–S_x and thus differences of the corresponding frequencies of the stretching vibrations in IR spectra. With the increase of the coordination number of the sulfur atom, the M–S distances expand and the M–S bonds weaken. The IR absorption around 900 cm^{-1} and those in the range of 400–525 cm^{-1} are attributed to ν(M–O_t) and the M–S stretching vibration [17,20–22], respectively. The increased bonding of the sulfur atom in the cluster compounds may result in an obvious red shift trend for the M–S stretching vibration. The M–S stretching vibration frequencies decrease in the order as follows: ν(M–S_t) > ν(M–μ_2-S) > ν(M–μ_3-S) > ν(M–μ_4-S). The M–S_t absorption is around 480–525 cm^{-1}, the 460 ± 15 cm^{-1} absorption is due to the ν(M–μ_2-S), the vibration frequency of M–μ_3-S equates to 445 ± 10 cm^{-1} and the ν(M–μ_4-S) is located in the region 440–420 cm^{-1}. For the isostructural Mo(W)/S/M′ cluster compounds, the M–S and M–O_t stretching vibration frequencies have the following order: ν(Mo–S) > ν(W–S), ν(Mo–O_t) < ν(W–O_t). This may indicate that there might be certain corresponding relationships between the structures of the heterothiometallic cluster compounds and the IR vibration frequencies of the different types of M–S.

According to these observations, we try to infer the core structures of the heterothiometallic cluster compounds containing the $[MXS_3]^{2-}$ moiety from their characteristic IR spectra with the M/M′ ratio determined by elemental analyses (EA) (M = V, Mo, W, Re; M′ = Cu, Ag, Au, Pd, Pt, Zn, Cd, Hg, Fe, Co, Ni, Sn).

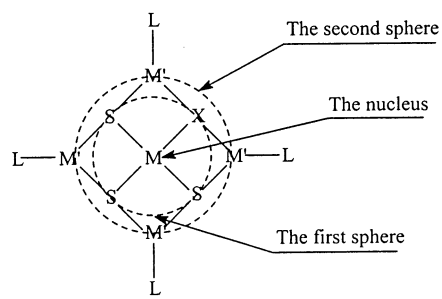
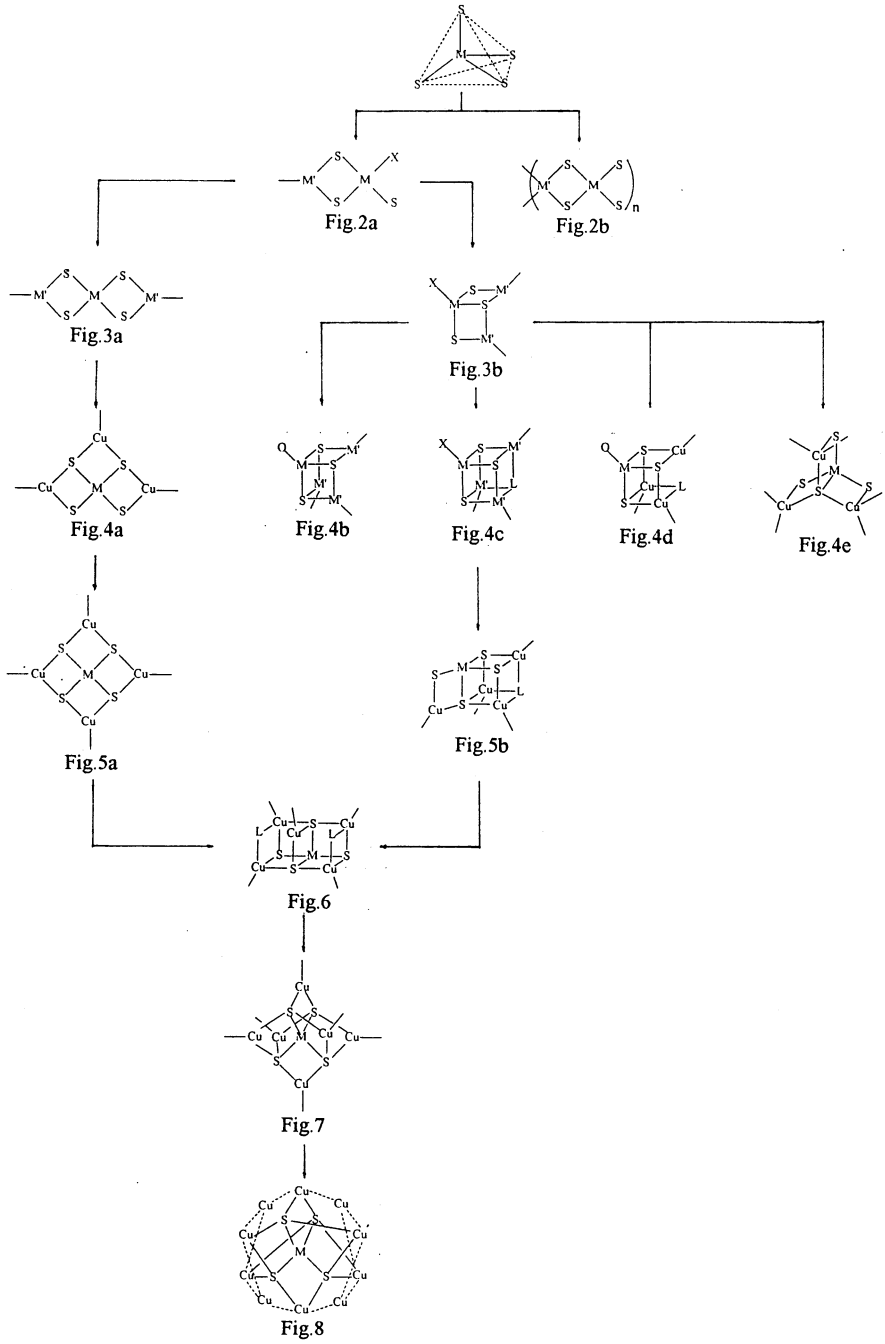
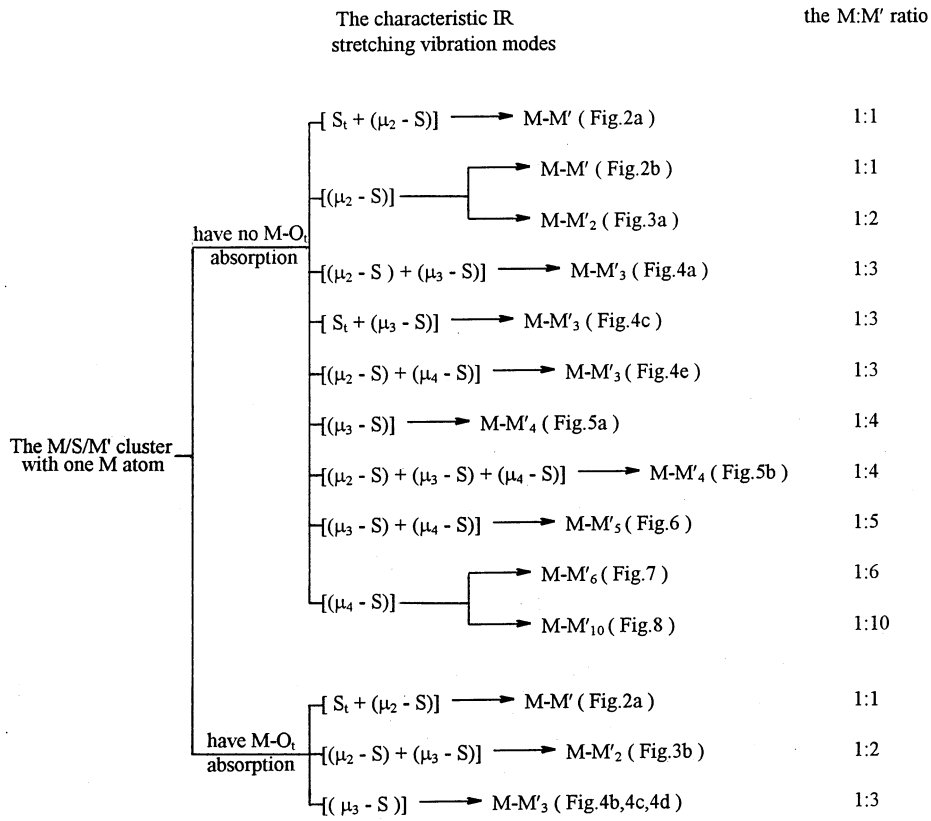


Fig. 1.



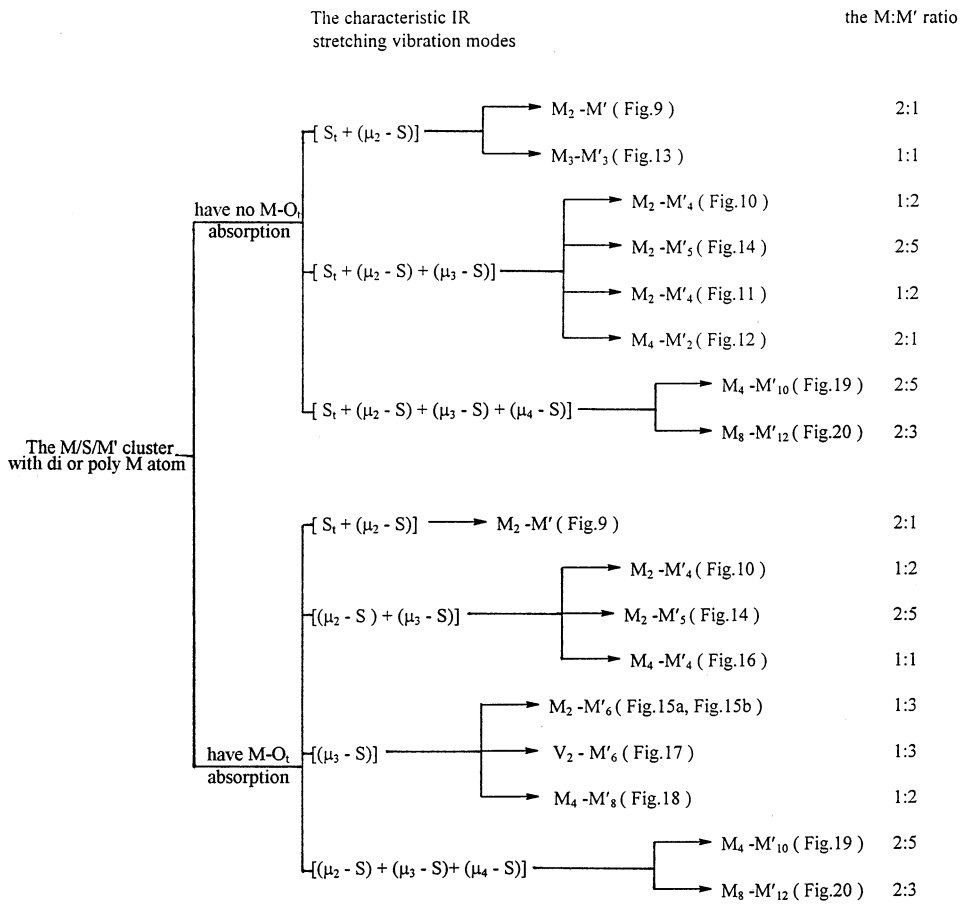
Scheme 1. The thirteen kinds of structural skeletons of the M/S/M′ heterothiometallic clusters with mono-M (M = V, Mo, W, Re) atom.



Scheme 2. The inferring procedure of the core structure of the M/S/M′ heterothiometallic clusters with one M atom by using the results of their IR and EA.

3. Classification and explanation

The existing M/S/M′ (M = V, Mo, W, Re; M′ = Cu, Ag, Au, Pd, Pt, Zn, Cd, Hg, Fe, Co, Ni, Sn) heterothiometallic clusters can be classified into three categories: $[MS_4M'_n]$ ($n = 1$–10), $[MOS_3M'_n]$ ($n = 1$–3) and $[M_m(XS_3)_a(S_4)_bM'_n]$ ($m = 2$–8, $n = 1$–12, $a = 0$–4, $b = 0$–4, X = O, S). The first two categories both contain one M atom. However, the second group $[MOS_3M'_n]$ ($n = 1$–3) can be distinguished from the first group $[MS_4M'_n]$ ($n = 1$–10) by having a M–O_t absorption band located in the range 880–940 cm^{-1}. The third category contains di- or poly-M heterothiometallic cluster compounds. Scheme 1 shows the thirteen well known kinds of structural skeletons of mono-M clusters. Schemes 2 and 3 illustrate the typical methods to predict the core structure of the M/S/M′ heterothiometallic cluster compounds with their preliminary configurations.



Scheme 3. The inferring procedure of the core structure of the M/S/M′ heterothiometallic clusters with di- and poly-M atoms by using the reults of their IR and EA.

3.1. The clusters containing one M atom and no O atom

The IR spectral parameters of the first group of clusters are shown in Table 1 and Table 4. There is no strong absorption M–O band ν(M–O_t) around 900 cm^{-1} for this kind of cluster. Further classification can be developed as follows:

Type of cluster	M/M′	Figure no.	ν (M–S_t)	ν (M-μ_2-S)	ν (M–μ_3-S)	ν (M–μ_4-S)	No. in table
Di-nuclear	1:1	2a	●	●			5–7, 46–49, 94, 95, 173–181, 185–199

		2b		●			3, 4, 44, 45
Tri-nuclear	1:2	3a		●			8–17, 50–54, 81, 96, 182–184
Tetra-nuclear	1:3	4a		●	●		25, 26, 64–67, 82, 83, 98
		4c	●		●		18–24, 55–62, 97
		4e		●		●	[a]
Penta-nuclear	1:4	5a			●		27–36, 68–74, 84–87
		5b		●	●	●	99
Hexa-nuclear	1:5	6			●	●	37, 38, 75, 76, 88, 100–102
Hepta-nuclear	1:6	7				●	39, 77, 78, 89–92
Undeca-nuclear	1:10	8				●	40, 41, 79

No IR results were reported [84].

3.2. The clusters containing one M atom and one O atom

The IR spectral parameters of the second group of clusters are shown in Table 2. There is a strong M–O absorption band $\nu(M–O_t)$ around 900 cm^{-1} for this kind of cluster. This is an obvious difference from those listed in Table 1. These clusters with five categories of skeletons are presented below:

Type of cluster	M/M′	Figure no.	ν ($M–O_t$)	ν ($M–S_t$)	ν ($M-\mu_2$-S)	ν ($M–\mu_3$-S)	No. in table
Di-nuclear	1:1	2a	●	●	●		105, 200
Tri-nuclear	1:2	3b	●		●	●	106–109, 128–130
Tetra-nuclear	1:3	4b	●			●	113, 116–118, 122, 137, 138
		4c	●			●	110–112, 119, 124, 125, 131–133, 136
		4d	●			●	114, 115, 120, 121, 123, 134, 135, 139, 140

Table 2
IR spectral parameters of the second category of the heterothiometallic cluster compounds

Number	Compound	M–O_t	M–S_t	M–μ_2-S	M–μ_3-S	M-μ_c-S	Symmetry group of core	Ref.
103	$[NH_4]_2[MoOS_3]$	835	485				C_{3v}	[23]
104	$[Et_4N]_2[MoOS_3]$	865	470				C_{3v}	[23]
105	$[Et_4N]_2[(CuCN)MoOS_3]$	893	499	462		424	C_s	[32]
106	$[(PPh_3)_3Cu_2MoOS_3]$	905		460	430	418	C_s	[88]
107	$[(PPh_3)_3Ag_2MoOS_3]$	914		460	443		C_s	[89]
108	$[(PPh_3)_2Py_2Cu_2MoOS_3]$	903		467	451		C_s	[90]
109	$[Et_4N]_2[MoOS_3Cu_2(S_2CNC_4H_8)_2]$	915		460	430		C_s	[21]
110	$[(PPh_3)_3Cu_3ClMoOS_3]$	908			451, 444		C_{3v}	[34]
111	$[(PPh_3)_3Cu_3BrMoOS_3]$	912			447		C_{3v}	[91]
112	$[(PPh_3)_3Cu_3IMoOS_3]$	910			445		C_{3v}	[91]
113	$[Bu_4N]_2[MoOS_3(CuNCS)_3]$	881			436		C_{3v}	[92]
114	$[Et_4N]_3[MoOS_3(CuI)_3(\mu_2\text{-}I)]\cdot H_2O$	911			442		C_{3v}	[91]
115	$[Et_4N]_3[MoOS_3(CuBr)_3(\mu_2\text{-}Br)]\cdot 2H_2O$	911			445		C_{3v}	[16b]
116	$[Bu_4N]_2[MoOS_3Cu_3BrCl_2]$	920			444		C_{3v}	[15b]
117	$[Py_5BrCu_3MoOS_3]$	925			445		C_{3v}	[93]
118	$[Py_5ICu_3MoOS_3]$	914			440		C_{3v}	[93]
119	$[MoOS_3Cu_3I(AsPh_3)_3]\cdot 2DMF$	920			446		C_{3v}	[94]
120	$[MoOS_3Cu_3(PPh_3)(S_2P(OBu)_2)]$	913.7			445.5		C_{3v}	[42]
121	$[MoOS_3Cu_3(PPh_3)_3(S_2COEt)]$	915			445		C_{3v}	[95]
122	$[MoOS_3Cu_3(SCN)Py_5]$	910.9			439.4	416.4	C_{3v}	[96]
123	$[(PPh_3)_3(CH_3COO)Cu_3MoOS_3]$	913			442		C_{3v}	[97]
124	$[MoOS_3Ag_3Cl(PPh_3)_3]$	930, 920			438		C_{3v}	[98]
124	$[Bu_4N]_3[Br_3Ag_3BrMoOS_3]$	907			438		C_{3v}	[99]
126	$[NH_4]_2[WOS_3]$	860	470				C_{3v}	[23]
127	$[Et_4N]_2[WOS_3]$	885	450				C_{3v}	[23]
128	$[WOS_3Cu_2(PPh_3)_4]$	896		472	443		C_s	[16a]
129	$[WOS_3Ag_2(PPh_3)_3]$	935		455	436		C_s	[89]
130	$[Et_4N][WOS_3(CuCN)Ag(PPh_3)_2]$	925		455	426		C_s	[100]
131	$[(PPh_3)_3Cu_3ClWOS_3]$	929			436		C_{3v}	[34]
132	$[(AsPh_3)_3Cu_3BrWOS_3]$	936			424		C_{3v}	[91]
133	$[(PPh_3)_3Cu_3IWOS_3]$	935			434		C_{3v}	[91]

Table 2 (*Continued*)

Number	Compound	M–O_t	M–S_t	M–μ_2-S	M–μ_3-S	M-μ_c-S	Symmetry group of core	Ref.
134	$[Et_4N]_3[WOS_3(CuBr)_3(\mu_2\text{-}Br)]\cdot 2H_2O$	914			435		C_{3v}	[16c]
135	$[Et_4N]_3[WOS_3(CuI)_3(\mu_2\text{-}I)]\cdot H_2O$	914			435		C_{3v}	[16d]
136	$[(AsPh_3)_3ICu_3WOS_3]$	935			434		C_{3v}	[91]
137	$[WOS_3Cu_3IPy_5]$	928			431		C_{3v}	[6d]
138	$[WOS_3Cu_3(SCN)Py_5]$	926.3			426.7		C_{3v}	[96]
139	$[WOS_3Cu_3(PPh_3)_3(S_2COEt)]$	930			440		C_{3v}	[10]
140	$[WOS_3Ag_3(PPh_3)_3(S_2P(OEt)_2)]$	942			446, 430		C_{3v}	[101]

Table 3
IR spectral parameters of the third category of the heterothiometallic cluster compounds

No.	Compound	M–O_t	M–S_t	M–μ_2-S	M–μ_3-S	M–μ_4-S	Symmetry group of core	Ref.
141	$[Et_4N]_2[Mo_2Cu_4S_8(S_2CNEt_2)_2]$		470	458	429		C_s+C_s	[21]
142	$[Mo_2Cu_4S_8(dppm)_2]$		472	458	437		C_s+C_s	[21]
143	$[(Ph_3P)_4Ag_4Mo_2S_8]$		515	453	438		C_s+C_s	[106]
144	$[Et_4N]_2[Mo_2Cu_5S_8(S_2CNMe_2)_3]\cdot 2H_2O$		513	455	444		C_s+C_{3v}	[107]
145	$[Bu_4N]_4[Mo_8Cu_{12}S_{32}]$		518	482	447	405	$4C_{3v}+4C_{3v}$	[108]
146	$[Bu_4N]_2[W_2Cu_4S_8(S_2CNC_4H_8)_2]$		495	450	435		C_s+C_s	[115]
147	$[(AsPh_3)_4W_2Ag_4S_8]$		511	469	434		C_s+C_s	[16e]
148	$[Bu_4N]_2[W_2Cu_5S_8(S_2CNMe_2)_3]$		495	448	425		C_s+C_{3v}	[116]
149	$[Bu_4N]_4[W_4Cu_{10}S_{19}]\cdot H_2O$		493.7	457.1	430.1	416.6	$2C_s+2C_{3v}$	[119]
150	$[Et_4N]_2[Mo_2Cu_5O_2S_6(S_2CNMe_2)_3]$	900		450	438		C_s+C_{3v}	[121]
151	$[Et_4N]_2[Mo_2Cu_5O_2S_6(S_2CNEt_2)_3]\cdot DMF$	905		450	435		C_s+C_{3v}	[121]
152	$[Et_4N]_4[Mo_2Cu_6O_2S_6I_6]$	913			447		$C_{3v}+C_{3v}$	[15d]
153	$[Et_4N]_4[Mo_2Cu_6O_2S_6Br_2I_4]$	901			447		$C_{3v}+C_{3v}$	[122]
154	$[Mo_2Cu_6O_2S_6(SCMe_3)_2(PPh_3)_4]$	920			450		$C_{3v}+C_{3v}$	[10]
155	$[Mo_2Ag_6O_2S_6(SCMe_3)_2(PPh_3)_4]$	930			490		$C_{3v}+C_{3v}$	[89]
156	$[Mo_2Cu_6O_2S_6(SCH_2CH_2OH)_2(PPh_3)_4]$	913			440		$C_{3v}+C_{3v}$	[123]
157	$[Et_4N]_4[Mo_4Cu_4O_4S_{12}]$	883.4		463	434		$4C_s$	[124]
158	$[Mo_4Cu_4O_4S_{12}(CuTMEN)_4]$	916			440		$4C_{3v}$	[124]
159	$[Bu_4N]_4[Mo_4Cu_{10}O_3S_{16}]\cdot H_2O$	894.8		462.8	453.2		$2C_s+2C_{3v}$	[119]
160	$[Bu_4N]_4[Mo_4Cu_{10}OS_{18}]\cdot H_2O$	894.8	505.3, 484	463	451.3		$2C_s+2C_{3v}$	[125]
161	$[Et_4N]_4[Mo_8Cu_{12}O_4S_{28}]\cdot DMF$	937.9, 894.4	486	468	449.8		$4C_{3v}+4C_{3v}$	[126]
162	$[W_2Cu_4O_2S_6(PPh_3)_4]$	937			438		C_s+C_s	[128]
163	$[W_2Cu_4O_2S_6(P(C_7H_7)_3)_4]$	940, 930		446	428		C_s+C_s	[129]
164	$[PPh_4]_2[W_2Cu_5O_2S_6(S_2CNEt_2)_3]\cdot DMF$	920		448	423		C_s+C_{3v}	[121]
165	$[W_2Cu_6O_2S_6(SCMe_3)_2(PPh_3)_4]$	940			460		$C_{3v}+C_{3v}$	[10]
166	$[W_2Ag_6O_2S_6(SCMe_3)_2(PPh_3)_4]$	949			425		$C_{3v}+C_{3v}$	[101]
167	$[Et_4N]_4[W_4Cu_4O_4S_{12}]$	902.6		488, 453	435.9		$4C_s$	[124]
168	$[W_4Cu_4O_4S_{12}(CuTMEN)_4]$	932			435		$4C_{3v}$	[124]
169	$[Bu_4N]_4[W_4Cu_{10}O_{2.5}S_{16.5}]\cdot H_2O$	914.1	495.6	453.2	426.2		$2C_s+2C_{3v}$	[125]
170	$[VOS_3(CuPBu_3)_2(CuSPBu_3)]_2$	958.5, 945			445.5		$C_{3v}+C_{3v}$	[130]
171	$[V_2O_2S_6(CuMeCN)_2(CuPPh_3)_4]$	954.7			449.9		$C_{3v}+C_{3v}$	[131]
172	$[V_2O_2S_6(AgPPh_3)_6]\cdot 2CH_2Cl_2$	957			447		$C_{3v}+C_{3v}$	[132]

Table 4
IR spectral parameters of the heterothiometallic cluster compounds containing M′ atom (M′ = Pd, Pt, Zn, Cd, Hg, Fe, Co, Ni, Sn, Ru)

No.	Compound	M–O_t	M–S_t	M–μ_2-S	M–μ_3-S	Symmetry group of core	Ref.
173	$[PPh_4]_2[I_2CdS_2MoS_2]$		498	440, 420		C_{2v}	[25]
174	$[PPh_4]_2[I_2HgS_2MoS_2]$		495	450		C_{2v}	[25]
175	$[PPh_4]_2[I_2ZnS_2MoS_2]$		500	460, 440		C_{2v}	[25]
176	$[(COD)PtMoS_4]$		506	468		C_{2v}	[26]
177	$[PPh_4][(PhCH_2)Me_3N][Cl_2FeMoS_4]$		504, 488	448		C_{2v}	[27]
178	$[Pr_4N][Ni(S_2CNEt_2)(MoS_4)]$		508, 500	468, 445		C_{2v}	[28]
179	$[Pr_4N][Pd(S_2CNEt_2)(MoS_4)]$		510, 503	458, 437		C_{2v}	[28]
180	$[Et_4N]_2[Cl_2Fe(MoS_4)]$		503, 488	452		C_{2v}	[29]
181	$[PPh_4][N(C_7H_7)Me_3][Cl_2FeMoS_4]$		496, 483.5	447.5		C_{2v}	[29]
182	$[Fe(DMF)_6][(FeCl_2)_2MoS_4]$			460		D_{2d}	[36]
183	$[PPh_4]_2[(FeCl_2)_2MoS_4]$			460		D_{2d}	[37]
184	$[Cp_2Ru_2(PPh_3)_2MoS_4]$			456		D_{2d}	[38]
185	$[PPh_4]_2[I_2CdS_2WS_2]$		495, 490	435, 430		C_{2v}	[25]
186	$[PPh_4]_2[I_2HgS_2WS_2]$		485, 480	440		C_{2v}	[25]
187	$[PPh_4]_2[I_2ZnS_2WS_2]$		490, 480	445		C_{2v}	[25]
188	$[PPh_4]_2[S_2NiS_2WS_2]$		527, 477	445		C_{2v}	[55]
189	$[(p\text{-Cymene})RuWS_4(PPh_3)]$		491	435		C_{2v}	[26]
190	$[(C_4Me_4)NiWS_4(PPhMe_2)]$		491	434		C_{2v}	[26]
191	$[(COD)PtWS_4]$		499	453		C_{2v}	[26]
192	$[NPr_4]_2[Ni(S_2CNEt_2)WS_4]$		492, 486	455, 448		C_{2v}	[28]
193	$[NPr_4]_2[Pd(S_2CNEt_2)WS_4]$		495	449, 443		C_{2v}	[28]
194	$[(Et_3P)_2PtS_2WS_2]$		498, 489	452, 435		C_{2v}	[56]
195	$[WS_4Pd(dppe)]$		530, 497, 482	441		C_{2v}	[57]
196	$[WS_4Pd(dppm)]$		545, 503, 495	440		C_{2v}	[58]
197	$[PPh_4]_2[Cl_2FeS_2WS_2]$		492, 482	443, 438		C_{2v}	[29]
198	$[Bu_4N]_2[(C_6F_5)_2PdS_2WS_2]$			460		C_{2v}	[59]
199	$[Bu_4N]_2[(C_6F_5)_4NiS_2WS_2]$			475, 465		C_{2v}	[60]
200	$[WOS_3Pt(PPh_3)_2]$	930, 910, 895	500, 490	450		C_s	[56]
201	$[PNP]_2[Et_4N][Fe(MoS_4)_2]$		495, 472	438		D_{2d}	[102]
202	$[Pr_4N]_2[Ni(MoS_4)_2]$		515, 499	454, 439		D_{2d}	[28]
203	$[Pr_4N]_2[Pd(MoS_4)_2]$		509, 494	450, 435		D_{2d}	[28]
204	$[Ph_4P]_2[Ni(MoS_4)_2]$		512, 499	455, 443		D_{2d}	[103]
205	$[Ph_4P]_2[Pd(MoS_4)_2]$		513, 497	450, 435		D_{2d}	[103]
206	$[Pr_4N]_2[Pt(MoS_4)_2]$		513, 497	459, 436		D_{2d}	[103]

Table 4 (*Continued*)

No.	Compound	M–O_t	M–S_t	M–μ_2-S	M–μ_3-S	Symmetry group of core	Ref.
207	$[Ph_4P]_2[Pt(MoS_4)_2]$		510, 496	454, 433		D_{2d}	[103]
208	$[Ph_4P]_2[Fe(MoS_4)_2]$		495, 472	438		D_{2d}	[104]
209	$[Ph_4P]_2[Zn(MoS_4)_2]$		516, 499	456, 435		D_{2d}	[105]
210	$[Et_4N]_2[Ni(WS_4)_2]$		499, 491	448		D_{2d}	[103]
211	$[Ph_4P]_2[Ni(WS_4)_2]$		498, 496	448		D_{2d}	[103]
212	$[Et_4N]_2[Pd(WS_4)_2]$		502, 492	439		D_{2d}	[103]
213	$[Ph_4P]_2[Pd(WS_4)_2]$		499, 491	440		D_{2d}	[103]
214	$[Et_4N]_2[Pt(WS_4)_2]$		500, 495	447, 440		D_{2d}	[103]
215	$[Ph_4P]_2[Pt(WS_4)_2]$		498, 491	447, 438		D_{2d}	[103]
216	$[Pr_4N]_2[Ni(WS_4)_2]$		497, 494	453		D_{2d}	[28]
217	$[Pr_4N]_2[Pd(WS_4)_2]$		502, 496	447		D_{2d}	[28]
218	$[Et_4N][PNP]_2[Co(WS_4)_2]\cdot 2CH_3CN$		476, 466	446, 438		D_{2d}	[109]
219	$[PNP]_2[Et_4N][Fe(WS_4)_2]$		470	431		D_{2d}	[110]
220	$[Ph_4P]_3[Fe(WS_4)_2]$		470	430		D_{2d}	[111]
221	$[Ph_4P]_2[Fe(WS_4)_2]$		493, 484	438		D_{2d}	[112]
222	$[Ph_4P]_2[Co(WS_4)_2]$		500, 491	450, 442		D_{2d}	[113]
223	$[Ph_4P]_2[Zn(WS_4)_2]$		492.4, 487.2	446, 435		D_{2d}	[104]
224	$[Ph_4P]_2[Cd(WS_4)_2]$		493, 486	435		D_{2d}	[114]
225	$[Ph_4P]_2[Hg(WS_4)_2]$		493, 486	431		D_{2d}	[114]
226	$[Ph_4P]_2[(NO)Fe(WS_4)_2]$		487	450, 443		D_{2d}	[112]
227	$[Ph_4P]_2[(DMF)_2Fe(WS_4)_2]$		484, 472	462, 446		D_{2d}	[114]
228	$[(PPh_3)N]_2[Et_4N]_2[W_3Fe_3S_{14}]$		480	443, 435		D_{3h}	[117]
229	$[Ph_4P]_4[(WS_4)_4Sn_2]$		491, 485	462, 440	434, 422	C_i	[118]
230	$[Ph_4P]_2[Ni(MoOS_3)_2]$	896, 884	500, 492	458, 446		D_{2d}	[120]
231	$[Ph_4P]_2[Zn(MoOS_3)_2]$	898	502	456, 437		D_{2d}	[120]
232	$[Ph_4N]_2[Ni(MoOS_3)_2]$	905	507	460, 448		D_{2d}	[28]
233	$[Ph_4N]_2[Pd(MoOS_3)_2]$	900	508	456, 440		D_{2d}	[28]
234	$[Ph_4N]_2[Pt(MoOS_3)_2]$	905	507	465, 440		D_{2d}	[28]
235	$[PPh_4]_2[Co(WOS_3)_2]$	917, 907	490, 485	445		D_{2d}	[127]
236	$[PPh_4]_2[Ni(WOS_3)_2]$	921, 908	496, 486	450		D_{2d}	[127]
237	$[PPh_4]_2[Zn(WOS_3)_2]$	918, 904	495, 485	440		D_{2d}	[127]
238	$[Ph_4N]_2[Ni(WOS_3)_2]$	913	496	454		D_{2d}	[28]
239	$[Ph_4N]_2[Pd(WOS_3)_2]$	917	497	444		D_{2d}	[28]
240	$[Ph_4N]_2[Pt(WOS_3)_2]$	915	490	451, 442		D_{2d}	[28]

The M/M′ ratio and the M–X (X = O_t, μ_3-S) stretching vibration frequencies of those clusters with the structures of Figs. 4(b,c,d) are similar. Differences in their structures can be found in the third sphere of their molecular space arrangement.

3.3. The clusters containing di- or poly-M atoms

The IR spectral parameters of the third group of clusters both with O atom(s) and with no O atom are located in Table 3 while M′ containing clusters (M′ = Pd, Pt, Sn, Fe, Co, Ni, Zn, Cd, Hg, Ru) are presented in Table 4.

3.3.1. Trinuclear clusters (two M atoms and one M′ atom) (M/M′ = 2:1) [28,102–105,109–114,120,127]

The structure mode for this group of clusters is linear (Fig. 9). Two kinds of characteristic IR vibration ν(M–X_t) and ν(M–μ_2-S) are considered in relation to two types of M–X bond, e.g. the M–X_t bond and M-μ_2-S bond in this group of clusters (X = O, S) (Table 4, nos. 201–227, 230–240).

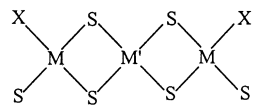


Fig. 9.

3.3.2. Hexanuclear clusters [16e,21,106,115,117,118,128,129]

Four types of structural fashion belong to this kind of cluster. The first type of cluster (Fig. 10) has two M atoms and four M′ atoms (M/M′ = 1:2) which can be considered as a combination of two butterfly-shaped units [$MXS_3M'_2$] (Fig. 3(b)).

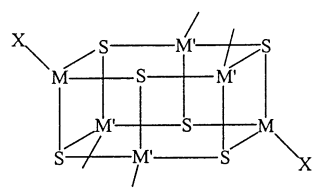


Fig. 10.

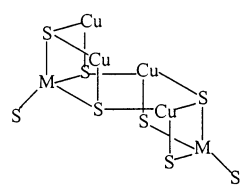


Fig. 11.

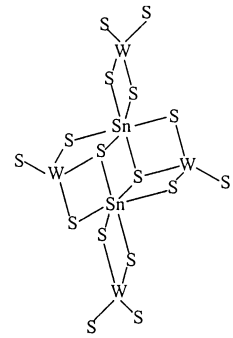


Fig. 12.

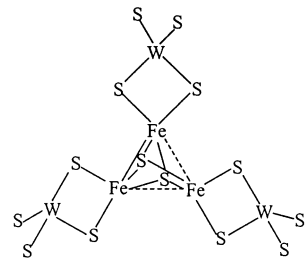


Fig. 13.

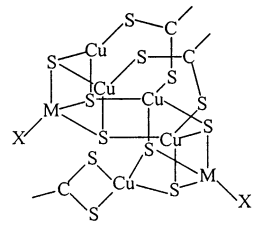


Fig. 14.

Therefore, three characteristic stretching vibration modes $\nu(M–X_t)$, $\nu(M–\mu_2\text{-}S)$ and $\nu(M–\mu_3\text{-}S)$ are exhibited in the IR spectra (X = O, S) (Table 3, nos. 143, 147, 162, 163).

In the second type structure (Fig. 11), which can also be divided into two butterfly-shaped units $[MX_tS_3M'_2]$ (Fig. 3(b)), three kinds of M–S bonds including M–S_t bonds, M-μ_2-S bonds and M–μ_3-S bonds lead to three types of characteristic IR absorption $\nu(M–S_t)$, $\nu(M–\mu_2\text{-}S)$ and $\nu(M–\mu_3\text{-}S)$ while the ratio of $M/M' = 1{:}2$ is determined by elemental analyses (Table 3, nos. 141, 142, 146).

The next two structural types, to our knowledge are only represented by one example, so far. The third type (Fig. 12), which may be regarded as consisting of two dinuclear units $[M(S_t)_2S_2Sn]$ (Fig. 2(a)) and two butterfly-shaped units

$[MS_tS_3Sn]$ (Fig. 3(b)), contains four W atoms and two Sn atoms (W/Sn = 2:1). Six W–S_t bonds, eight W–μ_2–S bonds and two W-μ_3-S bonds are formed with corresponding characteristic IR absorption bands (Table 4, no. 229).

Combining with three dinuclear units $[M(S_t)_2S_2Fe]$ (Fig. 2(a)), the fourth kind of cluster (Fig. 13) is constructed from three W atoms and three Fe atoms (W/Fe = 1:1) containing only W–S_t bonds and W-μ_2-S bonds. Two types of IR absorption ν(W–S_t) and ν(W-μ_2-S) contrast with two types of W–S bonds mentioned above (Table 4, no. 228). Both of these unusual heterothiometallic cluster compounds are easy to differentiate from other kinds of clusters by means of their IR and EA.

3.3.3. Heptanuclear clusters (two M atoms and five M′ atoms) [107,116,121]

This skeleton (Fig. 14) can be looked upon as being composed of one butterfly-shaped unit $[MX_tS_3M'_2]$ (Fig. 4(b)) and one nest-shaped unit $[MX_tS_3M'_3]$ (Fig. 4(b)) which leads to three kinds of stretching vibration frequency ν(M–X_t), ν(M–μ_2-S) and ν(M–μ_3-S) in correspondence with their characteristic IR spectra. Its M/M′ ratio equivalent to 2:5 is notable (X = O, S) (Table 3, nos. 144, 148, 150, 151, 164).

3.3.4. Octanuclear clusters [10,89,91,101,122–124,130–132]

There are three structural groups of compounds in these clusters. The first skeleton group (Figs. 15(a,b) consist of two half-open cubane-like units $[MOS_3M'_3]$ (Fig. 4(d)) or two nest-shaped units $[MOS_3M'_3]$ (Fig. 4(b)) with two M–O bonds and six similar M–μ_3-S bonds, giving rise to the characteristic ν(M–O_t) and ν(M–μ_3-S) vibration frequencies. It cannot be inferred that there are di- or poly-M atoms contained in these clusters only from the IR and EA results, because their IR and

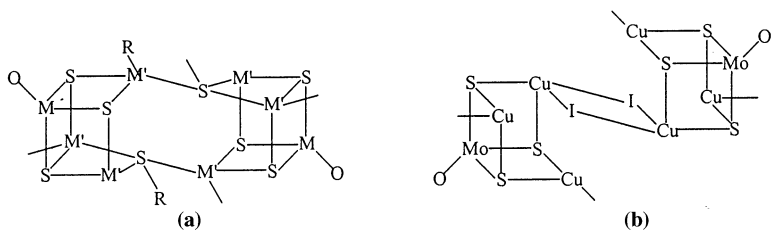


Fig. 15.

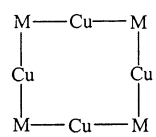


Fig. 16.

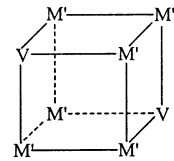


Fig. 17.

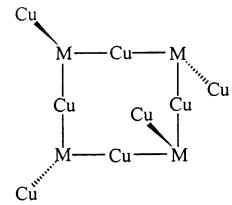


Fig. 18.

M/M′ ratio of 1:3 are very similar to those clusters shown in Fig. 4(d) or Fig. 4(b). The only conclusion that can be drawn is that there is a $[MOS_3M'_3]$ unit included in these clusters (Table 3, nos. 152–156, 165, 166).

The second cluster group (Fig. 16) may be treated as a composite of four butterfly-shaped units $[MOS_3M'_2]$ (Fig. 3(b)). Almost the same four M–O bonds, eight M–μ_2-S bonds and four M–μ_3-S bonds are expressed by three kinds of ν(M–O_t), ν(M–μ_2-S), ν(M–μ_3-S) stretching vibration modes while the M/M′ ratio equals 1:1 confirmed by elemental analysis, which hints that there are poly-M atoms and $[MOS_3Cu_2]$ units existing in these clusters (Table 3, nos. 157, 167).

The third type (Fig. 17) of structure has only been found in the V/S/M′ group of heterothiometallic cluster compounds. Dodecahedron-shaped clusters can be considered to be made up of two nest shaped units $[VOS_3M'_3]$ (Fig. 4(b)), which contain two V–O bonds and six V–μ_3-S bonds and lead to two kinds of ν(V–O_t) and ν(V–μ_3-S) stretching vibration modes (Table 3, nos. 170–172).

3.3.5. Dodecanuclear clusters (four M atoms and eight M′ atoms) [124]

Constituted from four similar nest-shaped units $[MOS_3M'_3]$ (Fig. 4(b)) sharing corners between each pair (Fig. 18), the four similar M–O_t bonds and twelve M–μ_3-S bonds exhibit the characteristic ν(M–O_t) and ν(M–μ_3-S) IR vibration frequencies. The IR and EA results suggest that this kind of cluster possesses di- or poly-M atoms with $[MOS_3M'_3]$ units (Table 3, nos. 158, 168).

3.3.6. Tetradecanuclear clusters (four M atoms and ten M′ atoms) [119,125]

Building with three kinds of unit such as two butterfly-shaped units $[MX_tS_3M'_2]$ (Fig. 3(b)), one nest-shaped unit $[MX_tS_3M'_3]$ (Fig. 4(b)) and one flywheel-shaped

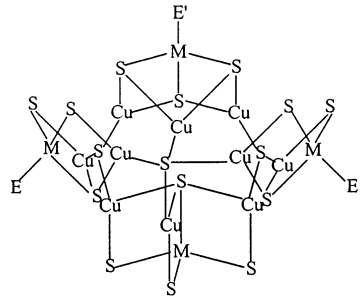


Fig. 19.

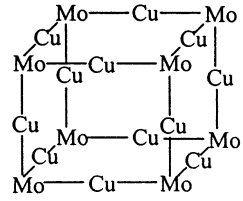


Fig. 20.

unit $[M(\mu_4\text{-}S)S_3M'_3]$ (Fig. 4(e)). The clusters (Fig. 19) have all four kinds of M–X bonds such as $M–X_t$, $M–\mu_2$-S, $M–\mu_3$-S and $M–\mu_4$-S, with characteristic $\nu(M–X_t)$, $\nu(M–\mu_2\text{-}S)$, $\nu(M–\mu_3\text{-}S)$ and $\nu(M–\mu_4\text{-}S)$ vibration modes. Their M/M′ ratio equals 2:5 (X = O, S) (Table 3, nos. 149, 159, 160, 169).

3.3.7. Eicosanuclear clusters (eight M atoms and 12 M′ atoms) [108,126]

This structure (Fig. 20) can be described formally as a supra-cubic cage formed by four nest-shaped units $[MX_tS_3M'_3]$ (Fig. 4(b)) and four flywheel-shaped units $[M(\mu_4\text{-}S)S_3M'_3]$ (Fig. 4(e)) with the metal atom coordinated through terminal X and μ_2, μ_3, μ_4 S bridging atoms. Characteristic $\nu(M–X_t)$, $\nu(M–\mu_2\text{-}S)$, $\nu(M–\mu_3\text{-}S)$ and $\nu(M–\mu_4\text{-}S)$ vibrations are located in the IR spectra. The M/M′ ratio is 2:3 which indicates the cluster must be a complicated molecule with poly-M atoms (X = O, S) (Table 3, nos. 145, 161).

Based on the classification and explanation above, one may find that the characteristic IR vibration frequencies of a cluster compound may correspond with two or more kinds of molecular structures in some cases. The correct structure can be further inferred from determining the M/M′ ratio by elemental analyses.

We illustrate three examples using IR spectra and EA to test and verify the conjecture methods listed in Scheme 2 and Scheme 3.

Example 1[46]:

$$(NH_4)_2MoS_4\ (1\ \text{mmol}) + \text{CuSCN}\ (4\ \text{mmol}) + \text{KSCN}\ (4\ \text{mmol}) \xrightarrow{\text{Py (20 ml)}} \text{Crystal } \mathbf{1}$$

Crystal **1** is synthesized by reacting 1 mmol $(NH_4)_2MoS_4$ with 4 mmol CuSCN and KSCN in 20 ml pyridine for ca. 30 min. Polyhedral crystals, black–red in

color, are obtained by diffusing dry Et_2O into the reaction filtrate. IR and EA measurement of the crystal are performed. No M–O_t absorption peaks appear and only one absorption peak is observed at 447 cm^{-1} which belongs to the Mo-μ_3-S stretching vibration. The Mo:Cu ratio equals 1:4. From these data we can reasonably infer its molecular core structure with moiety $[MoS_4Cu_4]$ as shown in Fig. 5(a).

Example 2[133]:

$$(NH_4)_2MoOS_3\ (1\ \text{mmol}) + CuI\ (3\ \text{mmol}) \xrightarrow[N_2]{\text{4-MePy (20 ml)}} \text{Crystal } \mathbf{2}$$

Crystal **2** is obtained by allowing 1 mmol $(NH_4)_2MoOS_3$ to react with 3 mmol CuI in 20 ml 4-picoline under an inert atmosphere. There are two obvious absorption bands at 910 and 437 cm^{-1}. They may be due to characteristic IR vibrations of Mo–O_t and Mo-μ_3-S, respectively. The Mo:Cu ratio is 1:3 with empirical formula $C_{36}H_{42}Cu_3IMoN_6OS_3$ according to elemental analyses. The core structure may be as shown in Figs. 4(b,c) with a $[MoOS_3Cu_3]$ unit by applying the methods in Scheme 2.

Example 3[134]:

$$(NH_4)_2WOS_3\ (1\ \text{mmol}) + CuI\ (3\ \text{mmol}) + \text{2-MePy}\ (5\ \text{ml}) \xrightarrow[N_2]{\text{DMF (5 ml)}} \text{Crystal } \mathbf{3}$$

The same procedure can also be used with crystal **3**. Two characteristic IR absorption bands at 917 and 437 cm^{-1} represent the W–O_t and W-μ_3-S stretching vibration modes. Thus crystal **3** has the structural framework displayed in Figs. 4(b,c) by utilizing the method mentioned in Scheme 2.

The core structures of the above three heterothiometallic cluster compounds have been determined by X-ray diffraction. The structures agree with the above analysis.

4. Discussion

A free $[MS_4]^{2-}$ anion with tetrahedral symmetry (T_d) possesses four internal vibrations: $T_d = A_1(\nu_1) + E(\nu_2) + 2F_2(\nu_3,\nu_4)$. Three of them $\nu_1(A_1)$, $\nu_2(E)$ and $\nu_3(F_2)$ are IR forbidden and inactive while only $\nu_4(F_2)$ species are active in IR. Therefore, only one absorption peak can be observed in the range from 400 to 500 cm^{-1}. In M/S/M′ cluster compounds, the $[MS_4]^{2-}$ moiety may have a lower symmetry. This leads to the splitting of ν_2, ν_3 and ν_4 [135,136] and additional vibrations will become IR active.

The free $[MOS_3]^{2-}$ anion has C_{3v} symmetry and six vibrations are expected: $C_{3v} = 3A_1(\nu_1,\nu_2,\nu_3) + 3E(\nu_4,\nu_5,\nu_6)$ [137]. Three of them [$\nu_3(A_1)$, $\nu_5(E)$ and $\nu_6(E)$] are in the far IR area, the others [$\nu_1(A_1)$, $\nu_2(A_1)$ and $\nu_4(E)$] are in the range of 400–1000 cm^{-1}. In M/S/M′ cluster compounds, the $[MOS_3]^{2-}$ moiety always has low symmetry. All of the transitions are IR active and ν_4(M–S)(E) exhibits splitting. There is a slight shift in the vibration position of ν_1(M–S)(A_1) because of the coordination with M′; the M–O bond length is shortened and the M–O_t stretching vibration band shifts to higher wave number. Further, three kinds of S atom (S_t, μ_2-S, μ_3-S) are formed. This results in a blue shift in the M–S_t stretching vibration band and a red shift in ν(M–μ_2-S) and ν(M–μ_3-S) compared with the original M–S vibration band.

1. The structural skeletons of Fig. 2(a) (X = S), Figs. 2(b), 4(a) and 6 are attributed to the C_{2v} symmetry group. Three kinds of vibration modes including $\nu_{as}(B_1)$, $\nu_{as}(B_2)$ and $\nu_s(A_1)$ are active in their IR spectra.

2. The structural type listed in Fig. 2(a) (X = O), Fig. 3(b) has C_s symmetry. Two types of stretching vibration $\nu_{as}(A')$ and $\nu_s(A')$ are displayed.
3. The cluster framework of Fig. 3(a), Fig. 9 belongs to the D_{2d} symmetry group. Two kinds of stretching vibration $\nu_{as}(B_2)$ and $\nu_{as}(E)$ appear in the IR range.
4. The structural arrangement of Figs. 4(b–e) can be assigned to the C_{3v} symmetry group. This causes two types of stretching vibration $\nu_{as}(E)$ and $\nu_s(A_1)$ in their IR spectra.
5. The structural mode of Fig. 5(a) which belongs to D_{4h} symmetry exhibits two IR active vibrations $\nu_{as}(E_u)$ and $\nu_s(A_{2u})$.
6. The cluster configuration of Fig. 7, Fig. 8 can be described by the T_d symmetry group. Only one kind of vibration mode $\nu_{as}(T_2)$ is revealed in their IR spectra.
7. The molecular structure of Fig. 5(b) has the C_1 symmetry group; structural symmetry is the lowest. One kind of stretching vibration is observed.

Actually, the IR spectra of the M/S/M′ heterothiometallic clusters are more complicated than considered above from their core structures. There are at least four factors inducing this complication:

4.1. Different coordination environments of sulfur atoms

There are several kinds of basic units in the clusters containing di- or poly-M atoms, in which, although the sulfur atom connection is the same, different sulfur atom coordination environments will give rise to shifts in the stretching vibration bands of M–S_x ($x = t$, μ_2, μ_3, μ_4). An example (Table 4. no. 229, Fig. 12) shows the characteristic IR absorption of the cluster but with two kinds of S_t and two kinds of μ_2-S arising from different coordination conditions.

4.2. Different d-electron configuration

The d-electron configuration of bivalent metal M′ atoms (e.g. Pd, Pt, Sn, Fe, Co, Ni, Ru) is different from that of univalent metal M′ atoms (e.g. Cu, Ag, Au). The heterothiometallic clusters containing the bivalent metal M′ atoms show a non-spherical symmetric distribution of their electron atmosphere, and the average M–S_x bond length ($x = t$, μ_2) shows small differences from those in univalent metal M′ atom clusters. The symmetry of their molecular space structure deviates from the D_{2d} or C_{2v} symmetry group and causes splitting in some IR absorption peaks as listed in Table 4.

4.3. Influence of periphery ligands

Although the characteristic IR spectra of the heterothiometallic clusters may be primarily determined by their core structure, the influences of the periphery ligands may not be negligible in some cases, such as in Table 1 nos. 33–35 (Fig. 5(a)). When the core structure [MS_4Cu_4] coordinates with a halogen anion Cl^-, its characteristic (μ_3-S) absorption is observed at 460 cm^{-1} only. However, when the

ligands are substituted by py or 4-pic, the characteristic IR peaks shift to 447 and 439.2 cm^{-1}, respectively.

4.4. Coupling vibrations

A new kind of coupling vibration mode ν(M-μ_c-S) may be found below 420 cm^{-1} mainly as a result of coincidence of the molecular vibration with the crystal lattice vibration (e.g. Table 1, no. 23 [$MoS_4Ag_3(PPh_3)_3(S_2P(OBu)_2)$]).

We would like to emphasize here again that only the M–S stretching vibration modes in the second sphere and the molecular arrangement within three spheres has been taken into account and used to analyze and infer the core structures of the heterothiometallic cluster compounds containing the $[MXS_3]^{2-}$ moiety.

5. Conclusions

On the basis of the classification, explanation and discussion given above, the following conclusions may be drawn:

1. There is a relationship between the molecular structures and the characteristic IR vibration frequencies in all of the M/S/M′ cluster compounds containing the $[MXS_3]^{2-}$ moiety.
2. There are several kinds of characteristic vibration modes including ν(M–S_t), ν(M–μ_2-S), ν(M–μ_3-S) and ν(M–μ_4-S). They are located in the range from 400 to 520 cm^{-1}.
3. Based on the study and analysis of the characteristic IR spectra and the M/M′ ratio of the heterothiometallic clusters, their core structure can be inferred.
4. The lower the symmetry of the cluster structures, the more splitting in their IR spectra. This is especially true for the more complicated core structure found in the clusters.
5. There are some rules in the characteristic IR frequencies of four groups (V, Mo, W, and Re) of heterothiometallic cluster compounds. The characteristic IR frequencies of the V and Re groups [ν(V–S_b) and ν(Re–S_b)] are higher than those of Mo and W groups [ν(Mo–S_b) and ν(W–S_b)]. In the isostructural Mo/S clusters and W/S clusters, ν(W–S_b) < ν(Mo–S_b), ν(W–S_t) < ν(Mo–S_t) and ν(W–O_t) > ν(Mo–O_t) are observed. Similarities can also be found between the isostructural Cu and Ag clusters as follows: ν(M–S_b(Ag)) < ν(M–S_b(Cu)), ν(M–S_t(Ag)) < ν(M–S_t(Cu)), and ν(M–O_t(Ag)) > ν(M–O_t(Cu)). Regarding the homologous M′ cluster compounds (M′ = Pd, Pt, Zn, Cd, Hg, Fe, Co, Ni,) the ν(M–S_x)(Pd), ν(M–S_x)(Pt), ν(M–S_x)(Ni) and ν(M–S_x)(Zn) are slightly higher than ν(M–S_x)(Cd), ν(M–S_x)(Hg), ν(M–S_x)(Co) and ν(M–S_x)(Fe) (M = Mo, W) (M–S_x ($x = t$, μ_2)).
6. Further investigation is needed to explain why the characteristic IR bands are split in the M′ containing (M′ = Zn, Cd, Hg) heterothiometallic clusters.

The characteristic IR spectra of these heterothiometallic clusters containing the $[MXS_3]^{2-}$ moiety is summarized as much as possible in this paper. All of the original IR data of the M/S/M′ clusters are collected and summarized directly from

the literature. Due to differences both in the IR instruments and in the choice of the intensity of the IR absorption peaks, there is still a slight difference between the IR data listed in the original literature and the IR absorption peaks predicted by us for a few of the clusters. We classify the IR absorption peaks of these heterothiometallic clusters, illustrate some regularities from their characteristic IR spectra, the core structure's symmetry, and the M and M′ ratio. This may open a very useful and convenient way to predict the primary structures of heterothiometallic clusters by using their characteristic IR spectra.

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