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Synthesis and characterization of an organic–inorganic hybrid compound: [WO_3 (2,2′-bipy)] (2,2′-bipy = 2,2′-bipyridine)

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The hydrothermal synthesis and characterization of an organic–inorganic hybrid compound [WO_3(2,2′-bipy)] (2,2′-bipy = 2,2′-bipyridine) is presented. This compound was characterized by various techniques including Raman and IR spectroscopy, XRD and thermogravimetric analysis. Structural analysis of the compound by Raman and IR data shows that it has a novel tungstate structure with 2,2′-bipy coordinated to tungsten. The X-ray powder diffraction data of the compound are indexed to a monoclinic cell with $a = 14.313(4)$, $b = 9.603(2)$, $c = 7.288(2)$ Å, $\beta = 102.07(2)°$. The structure of [WO_3(2,2′-bipy)] adopts a chain-like framework consisting of corner-shared distorted octahedra (WO_4N_2) with 2,2′-bipy acting as a bidentate ligand whose rings fan out from the chain. Upon heating, [WO_3(2,2′-bipy)] retains its structural integrity until 300 °C, followed by a gradual loss of 2,2′-bipy which leads to the formation of WO_3 at *ca.* 475 °C. The thermal decomposition is observed to proceed through a transitional intermediate, [W_4O_{12}(2,2′-bipy)], the structure of which is proposed and discussed.

Introduction

Recently, hydrothermal synthesis of novel metal oxides, using structure-directing agents, has attracted considerable interest owing to their potential applications in catalysis and material science as well as their rich structural chemistry.[1–3] For example, layered vanadium and molybdenum salts are formed using surfactant as structure-directing templates, under hydrothermal conditions.[4] By contrast, tungstate salts with Keggin-ion structure, *e.g.* [$(C_{12}H_{25}NMe_3)_6(H_2W_{12}O_{40})$] and [$(C_{16}H_{36}NMe_3)_6(H_2W_{12}O_{40})$], are formed with surfactant ions. Attempts to remove the surfactants from these tungstate salts by thermal treatment result in formation of tungsten oxides.[3,4]

Among the published studies so far, the role of aromatic amines appears to be relatively unexplored, and only a few studies involving molybdenum oxide or vanadium oxide, leading to compounds [MoO_3(2,2′-bipy)], [Mo_2O_6(2,2′-bipy)], and [Mo_3O_9(2,2′-bipy)$_3$];[5] [$VO(VO_3)_6(VO$(2,2′-bipy)$_2)_2$][6] and [V_3O_7(1,10-phen)][7] (2,2′-bipy = 2,2′-bipyridine, 1,10-phen = 1,10-phenanthroline) have been reported. No report with tungsten oxide has appeared in the literature. Furthermore, details concerning structural evolution upon removal of the aromatic amines from these vanadium and molybdenum compounds are, as yet, unclarified.[5–7]

Raman spectroscopy has been used not only for the characterization of a wide range of novel materials,[9–14] but also to delineate molecular speciation of tungstate ions in aqueous solution and on surfaces of supported WO_3 catalysts.[12–21] Moreover, 2,2′-bipy is also known to display distinct Raman features exhibited by various geometrical configurations.[22–27] Thus, Raman spectroscopy is capable of discerning molecular details of the synthetic, structural and mechanistic chemistry involving tungstates and 2,2′-bipy.

Here, we report on the synthesis and characterization of a novel organic–inorganic hybrid compound, [WO_3(2,2′-bipy)], as well as its structural evolution upon removal of organic template upon heating. This study is part of a research program aimed at the synthesis of novel organic–inorganic hybrid compounds *via* molecular architecture.[28,29]

Experimental

Preparation of [WO_3(2,2′-bipy)]

All the samples used in this study were obtained from commercial suppliers and used without further purification. H_2WO_4 (Strem), 2,2′-bipy (Fluka) and distilled water were first mixed, in a molar ratio of 1 : 2 : 700, in a 23 ml Teflon-lined acid digestion bomb (Hun Kung, Taiwan) and then heated at 160 °C for 96 h under autogeneous pressure. The resultant white solid (yield 80% based on tungsten) was filtered, washed with water and then air-dried for 12 h before subjecting it to further analytical studies.

Product characterization

Powder X-ray diffraction data were recorded at room temperature on a Siemens D5000 θ–θ diffractometer using Bragg–Brentano geometry with back-monochromatized Cu-Kα radiation. The diffraction pattern was scanned in steps of 0.02° (2θ) over the 2θ range 5–60° and a counting time of 5 s per step. The peak positions in the powder pattern were determined by means of the peak search routine in the PC software package DIFFAC-AT. The Raman spectrometer used in this study was a Renishaw system 2000 micro-Raman spectrometer equipped with a 25 mW He–Ne laser, operating at 632 nm, acting as the excitation source. A 5 μm exit slit offered a resolution of better than 1 cm^{-1}. *In-situ* Raman studies were carried out at a heating rate of 3 °C min^{-1} by use of a Linkam THM 600 heating cell up to the designated temperatures in air. FTIR spectroscopy was performed on a Perkin Elmer Paragon 1000 IR spectrometer with a resolution of 4 cm^{-1}, using KBr pellets. Thermogravimetry was conducted on a TA Instrument 2950 TG–DTA thermal analyzer using a heating rate of 3 °C min^{-1} in air. Chemical analysis for C, H and N was performed using an Heraeus elemental analyzer (Found: C, 30.66; H, 2.02; N, 6.99. Calc. for $C_{10}H_8N_2O_3W$: C, 30.95; H, 2.08; N, 7.22%).

Results and discussions

Fig. 1 shows the Raman spectra of solid 2,2′-bipy, H_2WO_4 and [WO_3(2,2′-bipy)] in the range 400–1700 cm^{-1} at room

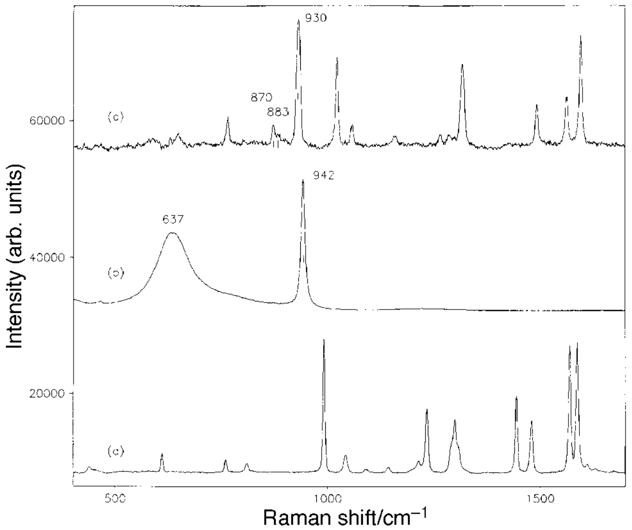

Fig. 1 Raman spectra of (a) solid 2,2′-bipy, (b) H_2WO_4 and (c) [WO_3(2,2′-bipy)].

temperature. The Raman spectrum of 2,2′-bipy [Fig. 1(a)] exhibits strong bands at 992, 1570 and 1588 cm^{-1}, medium bands at 1234, 1299, 1445 and 1480 cm^{-1}, and weak bands at 437, 610, 762, 811, 1042, 1090, 1143, 1215, 1289 and 1306 cm^{-1}.[22–24] The Raman spectrum of H_2WO_4 [Fig. 1(b)] exhibits a broad band centered at 637 cm $^{-1}$ and a sharp band at 942 cm^{-1}.[25] The product, [WO_3(2,2′-bipy)] [Fig. 1(c)], shows strong bands at 930, 1022, 1316 and 1595 cm^{-1}, together with medium and weak bands at 630, 650, 767, 870, 883, 1055, 1160, 1266 and 1290 cm^{-1}. The distinct Raman features of 2,2′-bipy, appearing in Fig. 1(a) and (c) (except for bands at 870, 883 and 930 cm^{-1}), are known to be associated with a transition from the *trans* form (C_{2h}) for the solid compound to the *cis* form (C_{2v}) in coordinated 2,2′-bipy.[24,26,27] The three Raman bands not associated with 2,2′-bipy, WO_3 and H_2WO_4 (at 870, 883 and 930 cm^{-1}), can be ascribed to W—O vibrations of the product. Fig. 2 shows the IR spectrum of [WO_3(2,2′-bipy)] in the range 500–1500 cm^{-1} at room temperature. Characteristic bands of H_2WO_4, a weak band at 940 cm^{-1} and a strong, broad band at 668 cm^{-1},[25] are not observed. In addition to bands due to 2,2′-bipy, strong bands at 934, 886, 617 cm^{-1} and a weak band at 860 cm^{-1}, are observed and can be ascribed to W—O vibrations of the product. Comparison of Fig. 1(c) and Fig. 2 with Raman and/or IR features of $H_2W_{12}O_{40}{}^{6-}$ and $WO_4{}^{2-}$-related compounds as well as a wide range of tungstates, in the range for characteristic W—O vibrations (600–1100 cm^{-1}), indicates that a novel tungstate structure is formed.[15–21] Moreover, the possibility of 2,2′-bipy being adsorbed on the surface of WO_3 can be excluded due to the complete absence of Raman features from WO_3,[18,19] despite the fact that H_2WO_4 transforms into WO_3 at around 160 °C.[31] Thus, Fig. 1(c) and 2 suggest the formation of a novel organic–inorganic hybrid compound which has the formula [WO_3(2,2-bipy)] as determined by elemental analysis. In order to explore the possibility of synthesis of compounds with different stoichiometries, a variety of synthetic variations were attempted. Despite adjusting the relative ratio of H_2WO_4 and 2,2′-bipy, varying the reaction duration and temperature (in the range 140–180 °C) or substituting H_2WO_4 by WO_3, only [WO_3(2,2′-bipy)] was formed under hydrothermal conditions, as identified by Raman spectroscopy. By contrast, [MoO_3(2,2′-bipy)] and [Mo_3O_9(2,2′-bipy)$_2$] could be synthesized by reacting MoO_3 with 2,2′-bipy whereas the synthesis of [Mo_2O_6(2,2′-bipy)$_2$] required the participation of cations.[5]

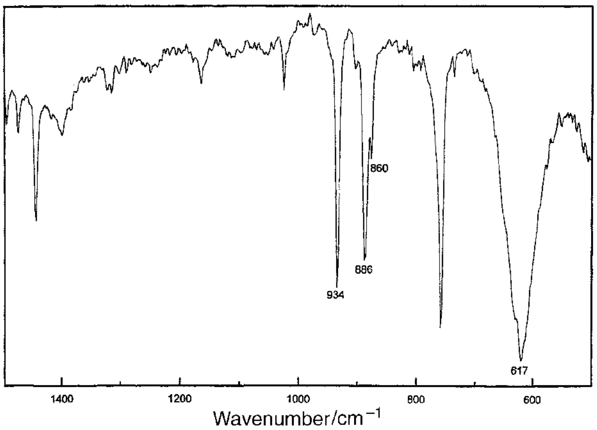

Fig. 2 IR spectrum of [WO_3(2,2′-bipy)].

The indexing of the X-ray diffraction powder pattern of [WO_3(2,2′-bipy)] was performed by using the program TREOR[30] which indicated a monoclinic system. The refined cell parameters were: $a=14.313(4)$, $b=9.603(2)$, $c=7.288(2)$ Å, $\beta=102.07(2)$ ° and $V=979.5$ Å^3. The corresponding figures of merit are $M_{20}=16$ and $F_{20}=31(0.0112, 58)$. The cell parameters are close to those of [MoO_3(2,2′-bipy)][5] and the indexed powder pattern is given in Table 1. The observed pattern of [WO_3(2,2′-bipy)] is in excellent agreement with the calculated powder pattern derived from the cell parameters and the atomic coordinates of [MoO_3(2,2′-bipy)],[5] indicating that the bulk product is monophasic and the two compounds are isostructural. Thus, a coordination environment with two terminal W=O bonds, two bridging W—O bonds and two W—N bonds, namely WO_4N_2, is ascribed to tungsten atom. Each octahedron establishes corner-sharing connections with two adjacent octahedra, through two bridging W—O bonds (W—O—W), to form an infinite chain-like framework with 2,2′-bipy fanning out along the chain.

In addition to XRD results, information concerning the coordination of tungsten and framework structure of

Table 1 Powder X-ray data of [WO_3(2,2′-bipy)]

h	k	l	I_{obs} (%)	d_{obs}/Å	$d_{calc}{}^a$/Å
1	1	0	100.00	7.905	7.919
2	0	0	24.09	6.993	6.998
0	2	0	13.19	4.797	4.802
3	1	0	23.15	4.197	4.197
2	2	0	14.76	3.958	3.959
−2	2	1	1.51	3.647	3.649
0	0	2	12.56	3.560	3.563
4	0	0	6.60	3.496	3.499
−1	1	2	16.85	3.401	3.404
3	1	1	1.06	3.352	3.351
2	2	1	1.60	3.299	3.299
1	3	0	6.82	3.118	3.120
−3	1	2	5.69	3.009	3.010
2	0	2	3.63	2.936	2.937
−1	3	1	1.00	2.908	2.909
0	2	2	4.73	2.861	2.862
4	2	0	4.23	2.826	2.828
5	1	0	6.31	2.689	2.688
3	3	0	5.08	2.640	2.640
−3	3	1	1.74	2.576	2.576
3	1	2	3.62	2.494	2.495
−4	2	2	2.93	2.423	2.424
0	4	0	1.83	2.401	2.401
−5	1	2	2.54	2.390	2.389
6	0	0	2.50	2.334	2.333
1	3	2	2.22	2.230	2.230
2	4	0	2.34	2.272	2.271
3	3	2	2.32	2.252	2.252

[a] Monoclinic, $a=14.313(4)$, $b=9.603(2)$, $c=7.288(2)$ Å, $\beta=102.07(2)$°, $\lambda=1.5406$ Å.

[WO_3(2,2′-bipy)] can also be obtained through analysis of vibrational features reported for a wide range of tungstates in the literature.[19–21] Geometries such as an isolated octahedron (Ba_2WO_6, R: 818 cm $^{-1}$ and IR: 620 cm^{-1}), a corner-shared octahedron (WO_3, R: 808 cm^{-1} and IR: 870 cm^{-1}) and an isolated tetrahedron (Na_2WO_4, R: 930 cm^{-1} and IR: 840 cm^{-1}) can be ruled out.[19,20] A distorted octahedral geometry with terminal W=O bonds, as found in $CdWO_4$ (R: 896 cm^{-1} and IR: 884 cm^{-1}) and H_2WO_4 (R: 948 cm^{-1} and IR: 948 cm^{-1}), appears more likely.[20,27] Raman bands at 930 and 883 cm^{-1} as well as IR bands at 934 and 886 cm^{-1} can be assigned to symmetric and asymmetric W=O stretchings[19–21] while the Raman band at 870 cm^{-1} and IR band at 860 cm^{-1} can be assigned to W—O stretching,[19–21] whereas the broad IR band at 617 cm^{-1} is assigned to W—O—W stretching.[21,25] In addition, three medium bands at 236, 260 and 360 cm^{-1}, and two weak bands at 300 and 320 cm^{-1} are also observed in the range 200–400 cm^{-1}. However, owing to their overlap with W—N stretching,[26,27] W—O bending, W—O—W deformation,[19–21] plus C–N and C–C torsion modes,[28] detailed assignment of these medium and weak bands cannot be made.

Fig. 3 shows the results of TG–DTG of [WO_3(2,2-bipy)], conducted at a heating rate of 3 °C min^{-1} in air. A sharp weight loss was observed between 300 °C and 450 °C with a plateau at 450 °C, corresponding to 60.5% of the original weight. This 39.5% weight loss corresponds to a stoichiometry of [WO_3(2,2′-bipy)$_{0.97}$], assuming loss of bipy and formation of WO_3 in good agreement with the formula determined by chemical analysis. Additionally, a DTG inflection around 410 °C corresponding to 69.3% of the initial weight (Fig. 3), suggests the formation of an intermediate with stoichiometry [W_4O_{12}(2,2′-bipy)] (*cf.* exptl. ratio W : bipy of 4 : 0.96) and *in situ* Raman studies were conducted to shed more light on this intermediate. Fig. 4 shows the *in situ* Raman spectra of [WO_3(2,2′-bipy)] heated to different temperatures, at a rate of 3 °C min^{-1} under ambient conditions. At 300 °C, Fig. 4(a) shows a spectrum almost identical to that in Fig. 1(c). At 350 °C [Fig. 4(b)], in addition to bands from [WO_3(2,2′-bipy)], two new bands emerge at 960 and 990 cm^{-1}. At 400 °C [Fig. 4(c)] these bands become prominent at the expense of the band at 930 cm^{-1}. At 475 °C [Fig. 4(d)] only two broad bands, centered at 700 and 800 cm^{-1}, can be observed indicating complete transformation into WO_3.[18] The results of the *in situ* Raman study are consistent with the thermogravimetric results (Fig. 3) and provide a more detailed molecular picture. For example, the observation of an identical spectrum at 300 °C to that at room temperature provides unambiguous evidence for the structural integrity of [WO_3(2,2′-bipy)] at this temperature. In contrast, either a significant degree of desorption of 2,2′-bipy or a strong fluorescence background is observed below 300 °C when 2,2′-bipy is adsorbed on surfaces of metal oxide supports.[32] It can be concluded that the stability of [WO_3(2,2′-bipy)] is dependent on that of 2,2′-bipy (bp = 273 °C) as well as the strength of bonding between the tungsten atom and 2,2′-bipy. Any attempt to isolate [W_4O_{12}(2,2′-bipy)] by careful thermal treament resulted only in the restoration of [WO_3(2,2′-bipy)], formation of WO_3 and unspecified amorphous species which were identified by thermogravimetric analysis, XRD and Raman spectroscopy (not presented here). The inability to isolate products other than [WO_3(2,2′-bipy)], either by thermal treatment or hydrothermal synthesis (*vide supra*), contrasts with the MoO_3–2,2′-bipy system for which stable [Mo_2O_6(2,2′-bipy)] and [Mo_3O_9(2,2′-bipy)$_2$] have been hydrothermally synthesized.[5] These two compounds exhibit chain-like frameworks similar to [MoO_3(2,2′-bipy)] in which the coordination of the molybdenum atoms varies, *viz.* 1 : 1 and 2 : 1, corner-shared octahedra (MoO_4N_2) and tetrahedra (MoO_4), respectively.[5] Since the intensity ratios of the 960 cm^{-1} band *vs.* the 990 cm^{-1} band at 350 °C [Fig. 4(b)] and 400 °C [Fig. 4(c)] remain essentially unchanged they can be ascribed to one species rather than a mixture of unspecified intermediates, with a coincident stoichiometry of [W_4O_{12}(2,2′-bipy)], the relative amount of which present would be temperature dependent.

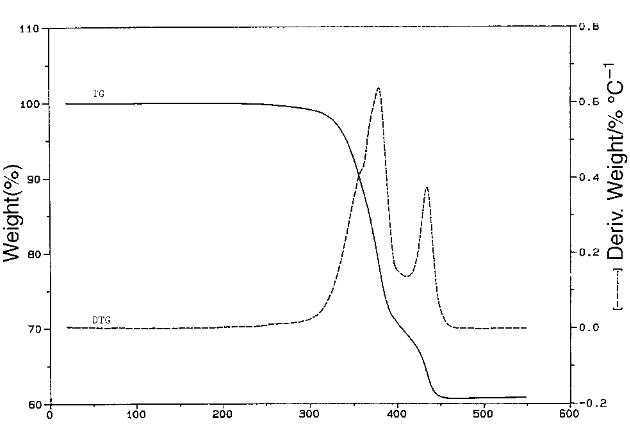

Fig. 3 Thermogravimetric analysis (TG and DTG) of [WO_3(2,2′-bipy)] at a heating rate of 3 °C min^{-1} under ambient conditions.

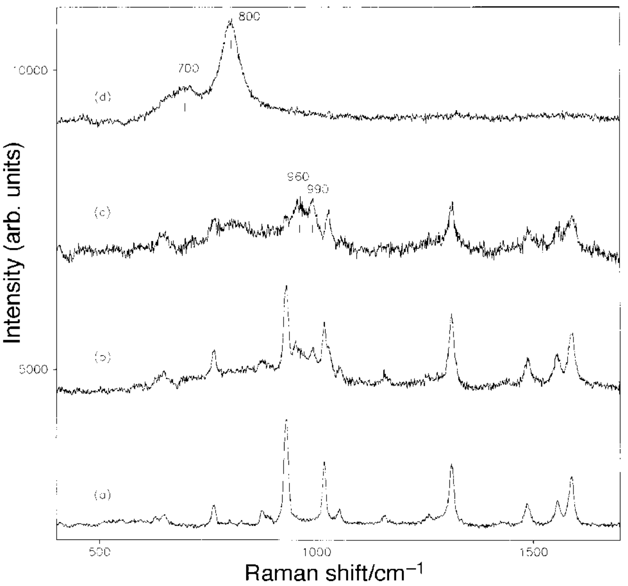

Fig. 4 *In situ* Raman spectra of [WO_3(2,2′-bipy)] at (a) 300 °C, (b) 350 °C, (c) 400 °C and (d) 475 °C, at a heating rate of 3 °C min^{-1} under ambient conditions.

Structural analyses on a wide range of tungstates indicate that the position of the Raman band with the highest wavenumber reflects, in general, the highest bond order in the sample.[14–21] For samples containing both tetrahedral and octahedral tungstates such as $Na_2W_2O_7$, assignments of characteristic bands for each geometry can be made.[33] Based on the structures of [WO_3(2,2′-bipy)], [Mo_2O_6(2,2′-bipy)] and [Mo_3O_9(2,2′-bipy)$_2$], the structure of [W_4O_{12}(2,2′-bipy)]can be tentatively proposed as follows. It most likely exhibits a chain-like framework as does [WO_3(2,2′-bipy)] consisting of octahedra (WO_4N_2) and tetrahedra (WO_4) in a 1 : 3 ratio. The band at 960 cm^{-1} can be assigned to a stretching vibration of W=O in octahedral geometry (WO_4N_2); and the band at 990 cm^{-1} can be assigned to a stretching vibration of W=O in tetrahedral geometry (WO_4). The shift from 930 to 960 cm^{-1} for the W=O stretching associated with octahedral geometry (WO_4N_2) can be explained in terms of the weakening of W—N bonding caused by heating above 350 °C, whereas a further shift from 960 to 990 cm^{-1} is a consequence of the complete absence of 2,2′-bipy in tetrahedral geometry (WO_4). However, the detailed structure of [W_4O_{12}(2,2′-bipy)] can not, as yet, be specified and more research is in progress.

Conclusion

Synthetic and X-ray structural details, vibrational and thermal properties of a novel organic–inorganic hybrid compound, [WO_3(2,2′-bipy)], are presented. The compound adopts a chain-like framework consisting of corner-shared distorted octahedra (WO_4N_2) with 2,2′-bipy acting as a bidentate ligand whose rings fan out from the chain. Upon thermal treatment, [WO_3(2,2′-bipy)] retains its structural integrity below 300 °C, and a transitional intermediate [W_4O_{12}(2,2′-bipy)] is identified around 410 °C before final conversion to WO_3 around 475 °C.

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