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## SPECTROSCOPIC INVESTIGATIONS OF $M(\text{CO})_5\text{-C}_{60}$ ( $M = \text{W}, \text{MO}$ ) COMPLEXES: PRECURSORS FOR METAL FULLERIDES

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### ABSTRACT

Photochemical reactions of  $M(\text{CO})_6$  ( $M = \text{W}, \text{Mo}$ ) with  $\text{C}_{60}$  in solution yield  $\eta^2$ -complexes of  $M(\text{CO})_5$  with  $\text{C}_{60}$ . The complexes have been characterised by IR, UV/VIS, NMR and DSC. They do not show any orientational ordering down to 12 K and all the infrared bandwidths remain the same down to this temperature. The complexes can be decomposed thermally or photochemically yielding metal fullerides, which show characteristic reduction in peak width in the variable temperature IR spectra due to orientational ordering. Transitions are manifested in calorimetric studies also. Metal  $\rightarrow \text{C}_{60}$  charge-transfer is observed in IR and XPS. A high temperature IR study of the  $\text{C}_{60}\text{-W}(\text{CO})_5$  complex reveals sequential elimination of the carbonyls yielding  $\text{MC}_{60}$ . The study shows that carbonyl complexes can be used as precursors to make transition metal fullerides.

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## INTRODUCTION

$C_{60}$ , the third allotrope of carbon, has many exciting features of which only a few are well studied. One such property is orientational ordering.  $C_{60}$  shows orientational ordering transition at 247 K which has been studied by calorimetric, spectroscopic and structural methods<sup>1-3</sup>. Because of the rapid spinning of  $C_{60}$  molecules in the lattice, to study its crystal structure it is desirable to freeze these motions. The discovery of various transition metal complexes in which the spinning motions are frozen due to complexation made the structure determination easier.  $C_{60}$  behaves as an electron deficient  $\pi$ -ligand which could readily bind to electron rich metal complexes, where metals are in their lower oxidation states. Thus, several Pt, Ir, Pd, Ru, Re and Fe complexes have been synthesized and characterised by NMR and X-ray crystallography<sup>4-9</sup>. But only a few W and Mo complexes of  $C_{60}$  have been reported so far. Tang *et al*<sup>10</sup> have synthesised and characterised the complexes  $[M(\eta^2-C_{60})(CO)_2(phen)(dbm)].C_6H_6.C_3H_{12}$  ( $M = W, Mo$ ) by chemical, spectroscopic and X-ray diffraction analysis. A molybdenum(0) complex,  $[Mo(CO)_3(DDH)]_3C_{60}.2.5C_6H_6$ , has also been reported in the literature<sup>11</sup>

The present study concerns with the photochemical reactions of  $C_{60}$  with transition metal carbonyls  $W(CO)_6$  and  $Mo(CO)_6$  yielding  $\eta^2$ -complexes. These complexes have both thermal and photochemical sensitivity and undergo facile decomposition to form metal fullerenes,  $MC_{60}$ . Spectroscopic and calorimetric studies confirm the

presence of orientational ordering in the decomposed samples whereas complexes manifest the change in their IR frequencies even at low temperatures. A detailed analysis of the decomposition pathway of the complexes has been carried out using variable temperature FT-IR spectroscopy.

## EXPERIMENT

Benzene solutions of C<sub>60</sub> and the transition metal carbonyls were mixed in a molar ratio of 1:5 and were irradiated with a xenon UV lamp (900 W) for about an hour. The mixture was periodically cooled to avoid thermal decomposition of the product formed. The green precipitate so obtained was centrifuged and washed with benzene and heptane in the order, to remove any excess unreacted carbonyl. It was then air-dried and the measurements were taken. For the temperature dependent IR studies, a 10% (by weight) pellet of the sample was made by mixing it with pure KBr powder. A Leybold commercial cryostat was used in association with a Perkin Elmer 983 IR spectrometer for low temperature measurements. The temperatures were set and allowed to stabilise before measurements. Averages of five scans were collected in the scan range of 300 to 2500 cm<sup>-1</sup>. The temperature range in which the measurements were done was from 12 K to 300 K. Spectra were recorded both for a fresh sample and for one that was exposed to light resulting in the loss of carbonyl groups. FT-IR studies were performed with a Bruker 66V FT-IR spectrometer and a variable temperature (298-500 K) accessory fabricated in our laboratory. To produce tungsten intercalated C<sub>60</sub> by a

different method, a stoichiometric mixture of  $W(CO)_6$  and  $C_{60}$  in an evacuated and sealed glass tube was heated to various temperatures ranging from 400 to 600 K affecting the decomposition of  $W(CO)_6$ . The UV/VIS absorption measurements were taken using a  $CS_2$  solution of the complex with a VARIAN CARY-05 spectrophotometer. The solutions upon prolonged standing decomposed to give parent  $C_{60}$  and a residue.

XPS measurements were conducted with a VG ESCALAB Mk II spectrometer with unmonochromatised Mg  $K\alpha$  radiation.  $^{13}C$  NMR measurement was done in a  $CS_2$  solution of the sample with  $Cr(acac)_3$  as the relaxation agent using a 20 mm probe of a 400 MHz GEOL NMR spectrometer. Differential Scanning Calorimetry thermogram was obtained with the DSC (+ +) instrument of Rheometric Scientific Ltd., and the samples were encapsulated in aluminium crucibles.

The synthetic methodology employed has been used earlier to prepare  $M(CO)_5$  complexes of Mo and W. For example, N,N'-thiobisamine complexes of the carbonyls were made by Diaz and Gonzalez by UV irradiation of THF solutions of  $M(CO)_6$  and amines<sup>12</sup>. Various phosphorous containing complexes of  $M(CO)_5$  ( $M = Cr, Mo$  and  $W$ ) were prepared by Brown and Dobson<sup>13</sup> following the UV irradiation method originally described by Strohmeier and Muller<sup>14</sup>

## RESULTS AND DISCUSSION

Detailed reports on the infrared spectra of the transition metal carbonyls illustrate the importance of this tool in arriving at the structural motif<sup>12,13,15-21</sup>

Almost all of the LM(CO)<sub>5</sub> complexes show four infrared bands assignable to the A<sub>1</sub> [two bands indicated as A<sub>1</sub>(1) and A<sub>1</sub>(2) in the literature], E and B<sub>1</sub> modes. The highest frequency band is assigned as A<sub>1</sub>(2) corresponding to the equatorial carbonyl stretching mode. The other A<sub>1</sub>(1) mode which generally occurs at the lowest frequency corresponds to the carbonyls in the equatorial plane<sup>16</sup>. There can be observable splitting of the E modes and consequently the infrared spectrum could consist of five bands in this region. Asymmetry in the lattice positions could lead to further splitting of certain modes. Infrared spectrum of the W(CO)<sub>6</sub> derived complex of C<sub>60</sub> is presented in Fig. 1 and the assignments are listed in Table 1. Carbonyl stretching region shown in the inset is in general agreement with the assignments presented in the literature and a molecular formula η<sup>2</sup>-C<sub>60</sub>W(CO)<sub>5</sub> can be suggested for the complex. The peak at 2086 cm<sup>-1</sup> is assigned to the equatorial C≡O stretching A<sub>1</sub> mode and that at 1928 cm<sup>-1</sup> is assigned to the equatorial C≡O A<sub>1</sub> mode. The highest intensity peaks at 1966 and 1952 cm<sup>-1</sup> are assigned to the E modes which are observed to have maximum intensity in these complexes. The asymmetry in the peak shapes is attributed to the solid state effects. The band at 1979 cm<sup>-1</sup> is assigned to the B<sub>1</sub> mode.

The above assignments are in accordance with IR spectra of LM(CO)<sub>5</sub> complexes reported in the literature. The W(CO)<sub>5</sub>-morpholine complex gives bands at 2078, 1985, 1945 and 1932 cm<sup>-1</sup> assigned to the A<sub>1</sub>(2), B<sub>1</sub>, E and A<sub>1</sub>(1) modes respectively<sup>12</sup>. W(CO)<sub>5</sub> complexes studied by Brown and Dobson gives

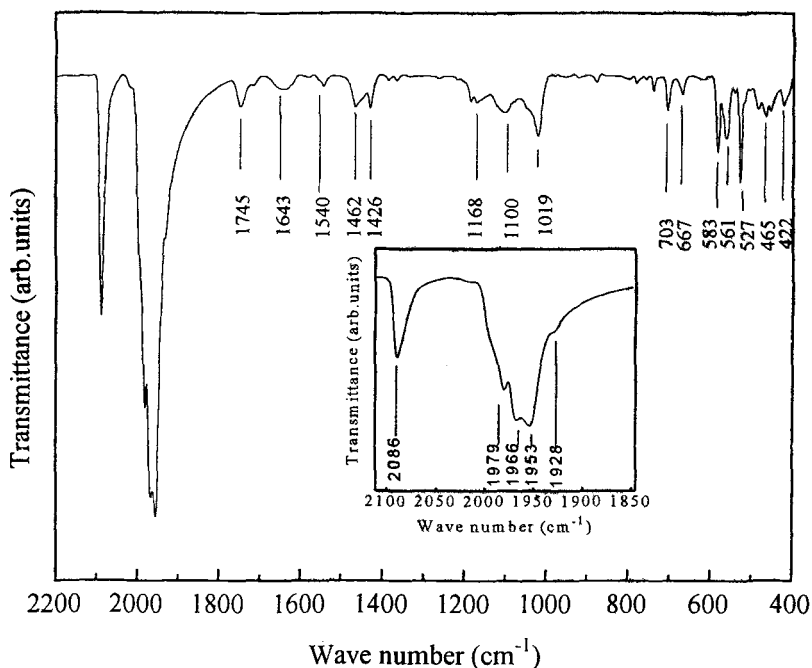


FIG. 1 Infrared spectrum of the  $C_{60}-W(CO)_5$  complex. The inset shows the  $C\equiv O$  stretching region. The important frequencies are marked.

bands around 2075, 1935, and 1920  $cm^{-1}$  and are attributed to  $A_1(2)$ ,  $E$ , and  $A_1(1)$  respectively<sup>13</sup>. The band profile obtained here is in accordance with the study of Cotton and Kraihanzel also<sup>15</sup>. The band around 1980  $cm^{-1}$  observed in the complexes is attributed to a  $B_1$  fundamental as in our case. In rigorous  $C_{4v}$  symmetry, the  $B_1$  mode is infrared inactive, but the true molecular symmetry is unlikely to be that. Therefore, it is very much likely that all the fundamentals become infrared active and true degeneracy of the  $E$  mode is removed explaining

Table 1. Infrared frequencies and assignments of the W(CO)<sub>5</sub>-C<sub>60</sub> complex.

Frequency (cm <sup>-1</sup> )	Assignments
2086	C≡O stretching of equatorial CO, A <sub>1</sub> (2) mode
1979	C≡O stretching, E modes
1966	
1953	C≡O stretching, B <sub>1</sub> mode
1928	C≡O stretching of equatorial CO, A <sub>1</sub> (1) mode
1540	Pentagonal pinch modes of C <sub>60</sub>
1462	
1426	
1168	C-C stretching of C <sub>60</sub>
1100	
1019	
875	
737	Vibrations of the fullerene framework
703	
667	
561	W-C≡O bending mode
583	Fullerene cage breathing modes
527	
483	W-C stretching modes
465	
451	
422	

the experimental data <sup>16</sup>. It may be added that the CO stretching region cannot be attributed to a M(CO)<sub>4</sub>L<sub>2</sub> complex where the range of carbonyl frequencies are shown to be much narrow <sup>15,17</sup>. Same is the case for M(CO)<sub>3</sub>L<sub>3</sub> and other substituted systems.



The low frequency region of the spectrum demonstrates the reduction of  $C_{60}$  symmetry where emergence of new bands occurs. The new peak at  $561\text{ cm}^{-1}$  and the cluster of bands in the range  $450\text{--}485\text{ cm}^{-1}$  are attributed to the complex formation. The cluster of bands at  $483$ ,  $465$ ,  $451$  and  $422\text{ cm}^{-1}$  are attributed to the W-C stretching modes. The band at  $483$  is tentatively assigned to the M-C stretch of the epical  $C\equiv O$ . One M-CO bending mode is observed at  $561\text{ cm}^{-1}$ . The  $C_{60}$  bands however, show only marginal shifts. The cage vibration of pristine  $C_{60}$  at  $575\text{ cm}^{-1}$  shifts to  $583\text{ cm}^{-1}$  whereas that at  $527\text{ cm}^{-1}$  remains at the same position. Near the pentagonal pinch mode of  $C_{60}$ , new bands occur at  $1540$  and  $1462\text{ cm}^{-1}$ . Similarly near the C-C stretch region new bands are observed at  $1168$  and  $1100\text{ cm}^{-1}$ . A cluster of new bands occur in the  $650\text{--}800\text{ cm}^{-1}$  region. These are attributed to the vibrations of the fullerene framework. The assignments listed here are also supported by the variable temperature data (see below). All the other spectral features are in close agreement with  $LW(CO)_5$  complexes<sup>12</sup>.

Very similar reaction was observed for  $Mo(CO)_6$  and the infrared spectrum in the CO stretching region of the  $C_{60}Mo(CO)_5$  complex is shown in the Fig. 2. Assignments can be made as in the case of the  $C_{60}W(CO)_5$  complex. However, the splitting of the E modes is not obvious as in the case of the W complex. The frequencies and band intensities are comparable to the  $C_{60}W(CO)_5$  complex.

The UV-Visible absorption spectrum of the complex in a  $CS_2$  solution is shown in Fig. 3. The spectra of  $C_{60}$  and  $W(CO)_6$  are also given for comparison.

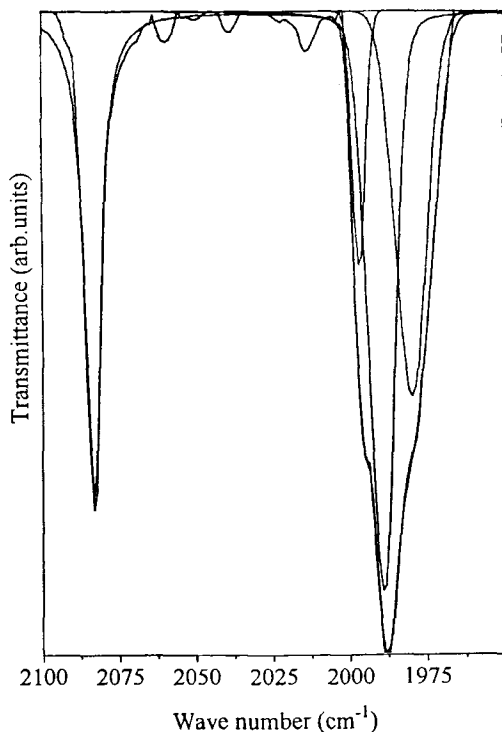


FIG. 2 C≡O stretching region of the infrared spectrum of the C<sub>60</sub>-Mo(CO)<sub>5</sub> complex. The spectrum has been deconvoluted to show the individual vibrations. There are three extra peaks which could be explained in terms of distortions in local symmetry.

The absorption spectrum in the low energy region is shown in the inset. All the absorption bands of C<sub>60</sub> are clearly discernable from the spectrum which shows characteristic red shift upon complexation. The absorption tail shifts to a longer wave length region and the first maximum is observed at 662 nm shifted from 620

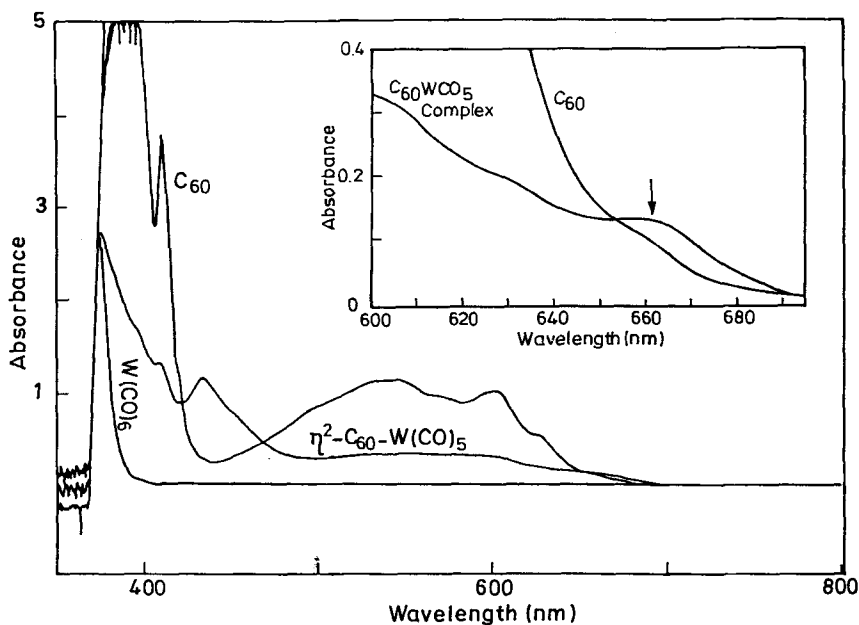


FIG. 3 Absorption spectra of  $C_{60}$ ,  $W(CO)_6$  and the  $C_{60}-W(CO)_5$  complex in  $CS_2$  solution. Inset shows a close-up of the 600-700 nm region.

nm of pure  $C_{60}$ . The characteristic metal-ligand charge transfer transition is observed at 434 nm. Similar transitions are observed in other transition metal- $C_{60}$  complexes<sup>10,11,22</sup>. This could explain the characteristic green colour of the complex which is a convenient way of assessing the complexation reaction.

Our attempts to crystallize the complexes were unsuccessful. For a complete characterisation, the  $^{13}C$  NMR spectrum in  $CS_2$  solution [with  $Cr(acac)_3$  as relaxation agent] was taken. The 100 Mhz  $^{13}C$  spectrum revealed three cluster

of resonances at 143.34, 133.16 and 130.2 ppm. An  $\eta^2$ -C<sub>60</sub> complex should show in 17 types of carbons <sup>4</sup> and these carbon positions in NMR vary substantially with the metal. Whereas in an iron complex <sup>19</sup> all these resonances appear in the range of 141-146 ppm, they occur in the range of 103-160 ppm in the osmium complex <sup>4</sup>

An earlier <sup>13</sup>C -MAS NMR study of a Mo(CO)<sub>3</sub>-C<sub>60</sub> complex shows four signals attributed to C<sub>60</sub> carbons in the range of 143-147 ppm <sup>11</sup>. No carbonyl peaks were observed in the spectrum. In the <sup>13</sup>C CP/MAS NMR ten C<sub>60</sub> peaks were observed <sup>11</sup> corresponding to C<sub>60</sub>. The observation seem to be similar in our case were also no carbonyl peaks are observed. Solid state <sup>13</sup>C NMR of Ta( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>) $\eta^2$ -C<sub>60</sub> <sup>9</sup> shows only a broad signal in the range of 141-145 ppm. These observations indicate the dependence of electron donor on the NMR spectrum and would suggest the fluxional nature of C<sub>60</sub> in the complex as suggested by Douthwaite *et al* <sup>9</sup>

Based on the spectroscopic data and an analysis of the W content in the sample by ICP-Atomic Emission Spectroscopy, we suggest a W(CO)<sub>5</sub>-C<sub>60</sub> stoichiometry for the complex and the proposed structure is given in Fig. 4. Earlier reports on the IR spectra of W(CO)<sub>5</sub>-C<sub>60</sub>, also suggest the same formula for the complex <sup>23, 24</sup>

In a temperature dependent IR study, we find that the infrared features do not manifest a change with lowering of the temperature unlike in the case of other C<sub>60</sub> derivatives studied in this laboratory <sup>25</sup>. The infrared spectra of W(CO)<sub>5</sub> in the

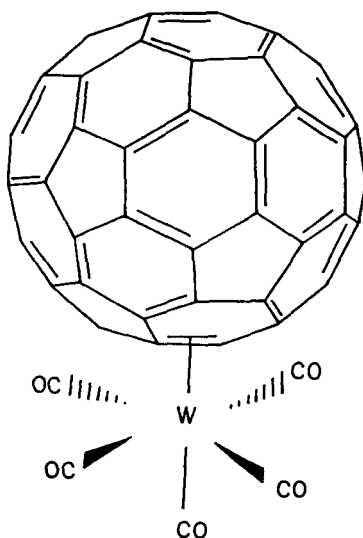


FIG. 4 Proposed structure of the  $C_{60}$ - $W(CO)_5$  complex. It is suggested that the metal atom binds to  $C_1$ - $C_2$  atoms between the hexagonal rings in an  $\eta^2$  fashion.

temperature range of 300-12 K are given in Fig. 5. The peak widths and positions do not manifest any change in this temperature range. The absence of such changes is particularly noticeable at the 1400-1500  $cm^{-1}$  region of the complex. Note that the pentagonal pinch mode of  $C_{60}$  is most sensitive to structural transitions. This spectral region is shown in Fig. 6a. To our surprise, a variable temperature study of the decomposed W complex showed drastic changes near the pentagonal pinch mode of  $C_{60}$  (Fig. 6b). Although no shift in the band position is observed, there is a sudden narrowing of the band indicative of phase transition. In

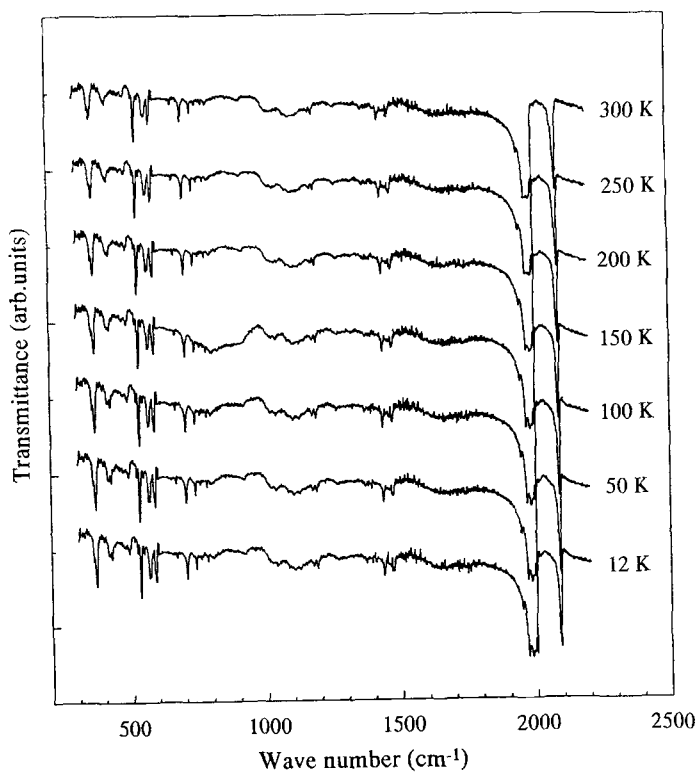


FIG. 5 Variable temperature IR spectra of the  $\text{C}_{60}\text{-W}(\text{CO})_5$  complex in the temperature range of 300-12 K. Note that no peak manifest change in width upon cooling.

Fig. 6c, we show the variable temperature spectra in the temperature range of 300-12K for the decomposed Mo complex. The same effect is seen here also. The marked narrowing of the bands suggests orientational disorder in the system. The presence of such disorder provides a vibrational relaxation pathway and consequently the life time of the vibrational mode decreases substantially leading to

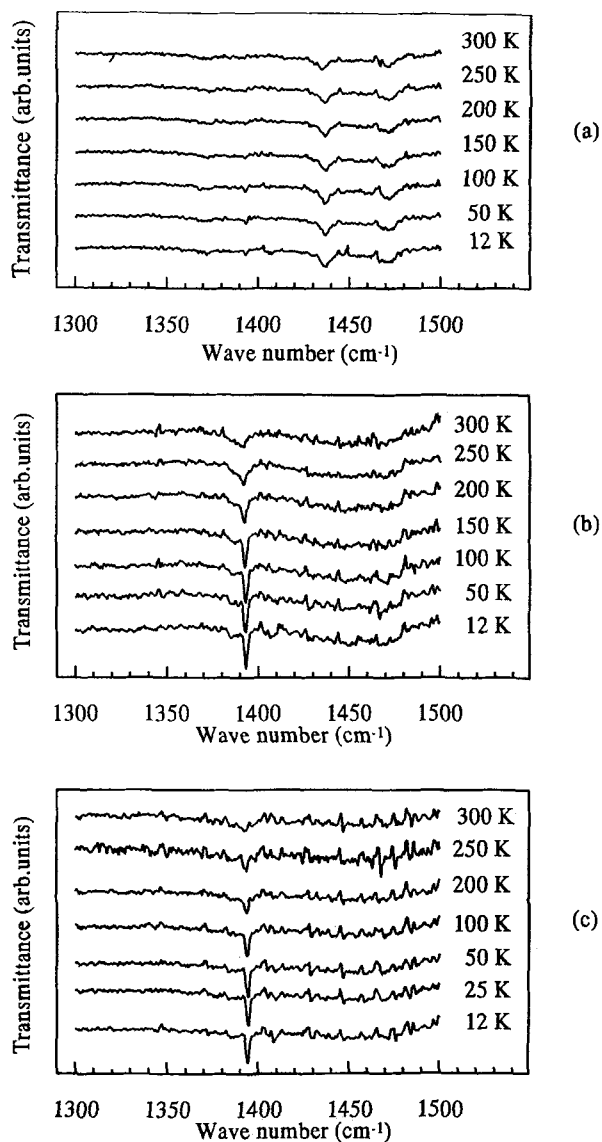


FIG. 6 Variable temperature IR spectra of the (a)  $C_{60}$ - $W(CO)_5$  complex (b)  $WC_{60}$  and (c)  $MoC_{60}$  in the temperature range of 300-12 K showing the pentagonal pinch mode of  $C_{60}$ .

a broad band profile. The variation of the bandwidth as a function of temperature for both the compounds are given in Fig. 7. Sudden change in bandwidth is indicative of a transition. In order to ascertain the structural transition, DSC measurements were carried out on the decomposed complexes. For WC<sub>60</sub>, two endothermal transitions at 259 and 294 K were observed with a  $\Delta H$  of 5.58 and 0.33 kcal/mg, respectively. The transitions for MoC<sub>60</sub> were observed at 246 and 291 K with a  $\Delta H$  of 1.88 and 0.29 kcal/mg, respectively. Both transitions appear to be orientational in nature from the low enthalpy values. They are not separately observed in the IR investigations as in the case of C<sub>60</sub> compounds studied by us earlier<sup>25</sup>. The  $\Delta H$  values and the corresponding transition temperatures from DSC measurements are given in Table 2.

The pentagonal pinch mode of C<sub>60</sub> in the decomposed complex appears at 1384 cm<sup>-1</sup>, down shifted by as much as 32 cm<sup>-1</sup> from pure C<sub>60</sub> corresponding to a metal fulleride formation. Assuming an 8 cm<sup>-1</sup> shift per electron transfer<sup>26</sup>, a transfer of four electrons could be inferred. The decomposed product is EPR active whereas carbonyl complex was diamagnetic. Our ICP-AES measurements reveal an approximately 1:1 stoichiometry for WC<sub>60</sub>. The DSC measurements also support the orientational ordering transition in the decomposed complexes.

In order to understand the nature of the valance states of these compounds, XPS measurements were undertaken. The XPS spectrum in the W 4f region of the decomposed W sample is shown in Fig. 8a. A binding energy of 32.0 eV for W



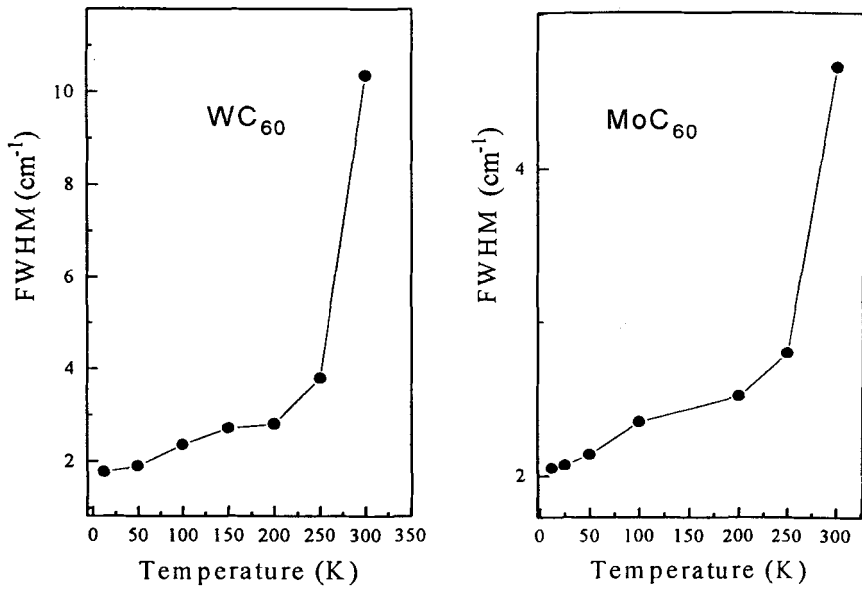


FIG.7 Shows the variation in the width of the 1384 cm<sup>-1</sup> band of the two compounds in the temperature region investigated.

Table 2. Transition temperatures and  $\Delta H$  values obtained from the DSC studies of MC<sub>60</sub>.

WC <sub>60</sub>		MoC <sub>60</sub>	
T <sub>c</sub> (K)	$\Delta H$ (mcal/mg)	T <sub>c</sub> (K)	$\Delta H$ (mcal/mg)
259	5.58	246	1.88
294	0.33	291	0.29

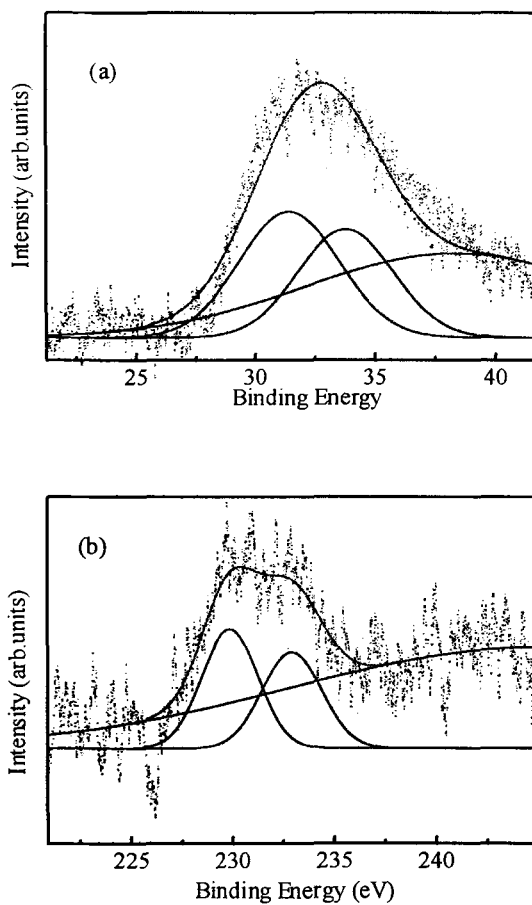


FIG. 8 X-ray photoelectron spectra in the (a) W 4f and (b) Mo 3d regions of the decomposed samples. The peaks have been fitted to symmetric Gaussians with approximate background subtraction. It is clear that only one kind of species contribute to the intensity in both the cases.

$4f_{7/2}$  is close to the value of 32.5 eV observed for WC<sup>27</sup>. In the Mo sample, Mo  $3d_{3/2}$  is observed at 229.5 eV (Fig. 8b) BE, higher than elemental Mo, but lower than MoO<sub>3</sub><sup>27</sup>. This BE is attributed to the Mo<sup>4+</sup>, in accordance with the IR data. The similar IR frequencies for the pentagonal pinch mode of C<sub>60</sub> for Mo and W samples suggest similar oxidation states for the two elements. However, the rather low value of the W  $4f_{7/2}$  BE is surprising for which we have no immediate explanation.

The decomposition pathway of the carbonyl complexes has been studied by temperature dependent FT-IR investigations of the  $\eta^2$ -C<sub>60</sub>W(CO)<sub>5</sub> complex. Upon increasing temperature, the carbonyl groups are eliminated in a sequential manner. This is manifested mainly in three regions of the spectra viz., 2200-1800 cm<sup>-1</sup>, 580-550 cm<sup>-1</sup> and 470-420 cm<sup>-1</sup>. The spectral regions which show changes correspond to C≡O stretching, W-(C≡O) bending and W-(C≡O) stretching vibrations. The bands corresponding to C<sub>60</sub> vibrations remain almost the same in intensity at higher temperatures. The variable temperature IR spectra in the C≡O stretching region are shown in Fig. 9a. At a temperature of 373 K, the equatorial C≡O stretching frequency [A<sub>1</sub>(2) mode] begins to lose intensity and correspondingly the equatorial C≡O mode [A<sub>1</sub>(1) mode] also reduces in intensity. At 473 K, these two modes completely disappear from the spectrum and the B<sub>1</sub> and E modes merge resulting in a broad band. It is important to observe that there is no shift in the peak positions. The changes occurring in the spectrum can be attributed to the

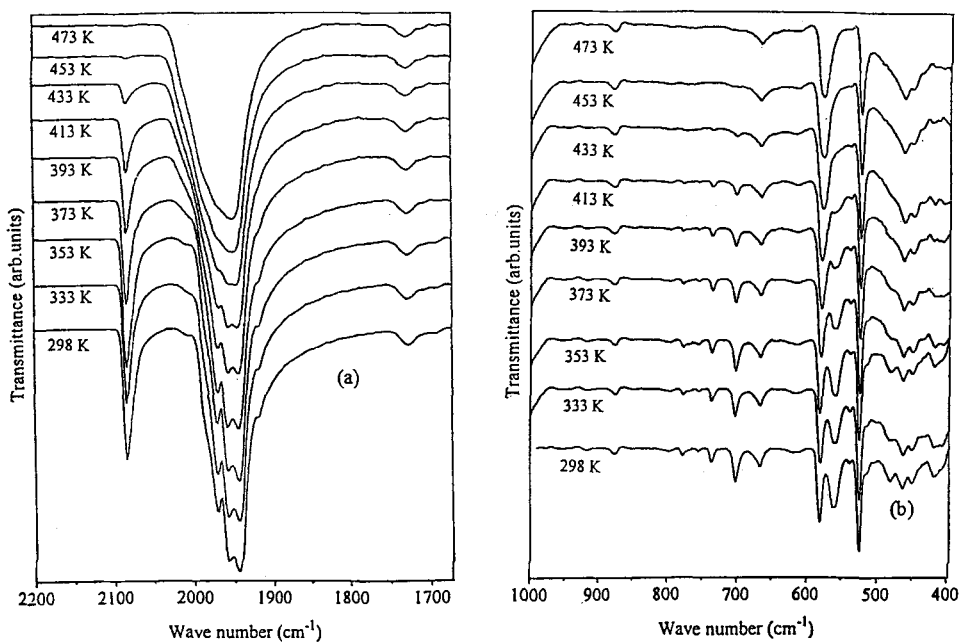


FIG. 9 Variable temperature IR spectra of the C<sub>60</sub>-W(CO)<sub>5</sub> complex in the temperature range of 473-273 K. The temperatures are labeled. (a) the C≡O stretching region and (b) the δ W-C≡O and γ W-C≡O region.

loss of carbonyls sequentially. Concordant with these changes, the low frequency region also manifests similar changes (Fig. 9b). Particularly interesting is the gradual disappearance of the W-C≡O bending mode at 561 cm<sup>-1</sup> and the disappearance of the W-C≡O stretching mode at 483 cm<sup>-1</sup>. These can be attributed to the faster loss of equatorial CO. Consequent to these changes, the C<sub>60</sub> bands at 583 cm<sup>-1</sup> broadens which may have contributions from W-C≡O bending modes from

the other carbonyl groups. The bands in the 650-800  $\text{cm}^{-1}$  region also change, which can be attributed to the changes occurring in the local symmetry of  $\text{C}_{60}$ . With increasing temperature, emergence of a new band with very weak intensity around 1400  $\text{cm}^{-1}$  is observed. This band can be attributed to the pentagonal pinch mode of the  $\text{C}_{60}$  of the fullerides, which showed maximum sensitivity for the phase transition involving orientational ordering of the  $\text{C}_{60}$  spheres. Due to limitations in the experimental set-up, temperature could not be increased further to effect complete decomposition.

The interstitial metallic compounds of the  $\text{C}_{60}$  with alkali and alkaline earth metals, where there is a donation of electrons from metal to  $\text{C}_{60}$ , are well studied<sup>28-31</sup>. But attempts to prepare metal fullerides with other metals have met with little success. Even though the LUMO of  $\text{C}_{60}$  lies deeper than the Fermi level of the transition metals and there is no barrier for charge donation, the fundamental limitation for the intercalation and fulleride formation is to overcome the cohesive energy of the metal<sup>32</sup>. As an attempt to prepare transition metal fullerides, the thermal decomposition methods were used. The materials prepared by the thermal decomposition of  $\text{W}(\text{CO})_6$  in presence of  $\text{C}_{60}$  at various concentrations and temperatures are found to be substantially different from the fullerides formed from the complexes. No significant shift is observed in the pentagonal pinch mode of  $\text{C}_{60}$  appearing at 1428  $\text{cm}^{-1}$  in the IR spectra of these materials, suggesting the absence of substantial electron transfer. It is important to note that the metal

fullerides formed by the decomposition of M(CO)<sub>5</sub>-C<sub>60</sub> are compounds in which electron transfer is observed. It is unclear as to how the difference in the charge states occur between two different preparative procedures. It appears that the complexation with metal and subsequent elimination of the carbonyls leave the metal centre in close proximity to C<sub>60</sub> to affect electron transfer. What turns out from this study is that metal fullerides can be prepared from M(CO)<sub>5</sub>-C<sub>60</sub> precursors. The compounds so prepared are stable enough for detailed spectroscopic characterisation.

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