Synthesis and characterization of nicotinic acid coordinated metal carbonyl complexes

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Two zero-valent metal carbonyl complexes fac-[M(CO)3(L)(NIC)] (where M = Mo, W; 3, 4; NIC = 3-HO2CC(=N)H) have been synthesized and characterized by elemental and thermal analyses (TGA, EGA), IR and powder X-ray diffraction (XRD) spectroscopic techniques. The IR spectrum of complex 3 exhibits three CO stretching bands and 4 shows two CO stretching bands in addition to a carboxyl-carbonyl stretching band. The possibility of fac/mer isomerization in complex 3 has been studied by IR spectroscopy in various solvents. Elemental and mass-spectrometric data are consistent with the formulae of the title complexes. The powder X-ray diffractogram of complexes 3 and 4 exhibit similar pattern suggesting the same geometry.

Nicotinic acid (NIC) has been found to be one of the essential constituents1 for human pellagra-preventing (P-P) factor. It is present in the RBC's of blood2 as its coenzymes NAD and NADP. The rapid growth of organo-transition metal carbonyl complexes with ligands of biological origin3 and their important applications have been reviewed4. The incorporation of NIC as ligand in various metal carbonyls and study of their coordination chemistry and structure are of immense interest since metal carbonyl complexes with biologically important ligands find applications in carboxymetalloimmunoassay (CMIA), a non-isotopic immunological method5,6. NIC has also been used7 as a versatile ligand for the preparation of a number of 99mTe-labeled complexes for radiopharmaceuticals. Moreover, the title complexes are used to prepare water-soluble analogues8,9.

Metal carbonyl complexes of the type M(CO)3L3 (M = Cr, Mo and W) where L denotes various group VA donor ligands have been prepared10 and their IR spectra and bonding have been studied11. The presence of “M(CO)5” fragment in group VB metal carbonyl complexes with various mono- and polydentate ligands in various chemical environments have also been reported12-21. The species fac-[M(CO)3(CH3CN)2] (M = Cr, Mo and W) were found to be good complex precursors for the preparation of new complexes17 not easily made by other synthetic routes. Only few complexes have been synthesized utilizing these intermediate fragments18-21. In order to explore the synthetic utility of these complex precursors, we report the preparation, properties and characterization of two metal carbonyl complexes 3 and 4.

Experimental
All reactions were carried out in a Schlenk line under an atmosphere of purified dry argon. All the solvents were purified by standard methods22 and purged with argon before use. Molybdenum hexacarbonyl (MERCK) and Tungsten hexacarbonyl (Aldrich Chemical Co.) were used without further purification. NIC was recrystallised from ethanol.

Elemental analyses (C, H and N) were carried out using a Heraeus CHN-O rapid elemental analyzer. FAB-MS was carried out on a VG 70-70H spectrometer. FT-IR spectra were recorded on a Bruker IFS 66V FT-IR spectrometer. TGA was carried out on a Perkin-Elmer TGA 7 thermogravimetric analyzer. EGA was carried out on a Balzers GAM 440 evolved gas analyzer. UV-Vis spectra were recorded on a Perkin-Elmer Lambda 17 UV/Vis spectrophotometer.

Powder X-ray diffraction (XRD) patterns were obtained at room temperature using a Rigaku miniflex X-ray diffractometer. The XRD pattern of complex 3 was recorded using Fe filtered Co-Kα (λ = 1.7902 Å) radiation. The XRD pattern of complex 4 was recorded using V filtered Cr-Kα (λ = 2.291 Å) radiation. The 20 angle was scanned at a rate of 2° min-1.

Preparation of complexes
The title complexes 3 and 4 were prepared in a two step synthetic procedure (Scheme 1). In the first step, the tris-acetonitrile substituted complexes fac-[Mo(CO)3(CH3CN)2] (1) and fac-[W(CO)3(CH3CN)2] (2) were generated17 under ‘in situ’ conditions as complex precursors. The complexes 1 and 2 are highly sensitive to air and moisture and strict inert atmosphere was maintained throughout the reaction. fac-[Mo(CO)3(NIC)] (3)

Mo(CO)6 (0.25 g, 0.9469 mmol) dissolved in 20 ml of CH3CN was allowed to reflux for 8 h to generate 1. The solution of 1 was cooled to room temperature and treated with three equivalents of NIC (0.3497 g.
Results and discussion

Both the complexes are air sensitive and need to be stored under inert atmosphere. Complexes 3 and 4 are both insoluble in most of the common solvents (water and organic) employed but sparingly soluble in dimethyl sulfoxide and tetrahydrofuran. In these two solvents, the complexes are decolourized and decompose upon dissolution. Analysis of the IR and UV-Vis spectra of the solution do not give useful information on structure. The IR spectrum of complex 3 in DMSO does not show carbonyl stretching in CO region. UV-Visible spectrum shows band(s) corresponding to pure NIC only. The highly air-sensitive nature of the complexes in solution and the simultaneous decomposition of the complexes make it difficult to study the properties of these complexes in solution. Hence our attempts to grow single crystals for X-ray crystallographic studies of complexes 3 and 4 were unsuccessful.

$\text{FT-IR spectral and stereochemical studies}$

The IR spectrum (KBr pellet) of complex 3 shows three strong carbonyl stretching bands at 1904, 1799 and 1769 cm$^{-1}$ and a band of medium intensity at 1703 cm$^{-1}$ assigned to carboxylic carbonyl ($v(C=O)$) stretching. Complex 4 exhibits two strong carbonyl stretching bands at 1892 and 1760 cm$^{-1}$ and a strong $v(C=O)$ stretch due to carboxylic carbonyl at 1710 cm$^{-1}$. The observation of single peak at 1703 cm$^{-1}$ for complex 3 and 1710 cm$^{-1}$ for complex 4 suggests the coordination of three molecules of NIC at the metal centres.

The carbonyl stretching bands in the C–O region suggest three mutually cis-carbonyl groups$^{10}$. The appearance of three carbonyl stretching bands in complex 3 could be due to change in the geometry from facial to meridional. Although it is possible to predict the geometry of complexes based on the number of observed carbonyl stretching bands, the electronic factors should not be ignored. Hence the nature of the ligand viz., donor-acceptor properties, bonding and orientation in the crystal lattices should also be taken into consideration.

Large number of complexes of group VIB metal carbonyls exhibit three or more number of carbonyl stretching bands in the facial arrangement$^{10,23}$, contrary to the expected number of two bands for $C_{3v}$ symmetry. This is due to the reduction in the Lewis acidity of the metal by the incorporation of strong σ-donating ligands$^{23}$ which in turn decreases the metal-carbon bond strength of each coordinated carbonyl in the metal complex and weakens the M–C bond. As a result, this leads to greater interaction of three CO groups with the metal in the crystal lattices. This is more so in the molybdenum complex than in tungsten complex, because of large variations in the periodic properties$^{24}$ of molybdenum and tungsten. The observation of three carbonyl bands in complex 3 in contrast to two bands in complex 4 could be explained on this basis. Moreover, metal carbonyl complexes in the solid state exhibits more number of $v(C=O)$ bands than the symmetrically allowed vibrations. This is due to the difference in symmetry possessed by a complex.
in the solid state and symmetry of the crystal and also the intermolecular interactions between CO groups. The appearance of broad bands in complex 4 is not unusual in solid state spectra of tungsten complexes. Therefore, it is difficult to assign the structure from the spectra of solid complexes. If the complexes 3 and 4 have meridional geometry, this will be reflected in the number and position of v(C=O) pattern and the carboxylic carbonyl v(C=O) pattern. In both the cases, we observed a single v(C=O) for NIC suggesting coordination of three NIC in the cis-manner. This suggests the C₈ configuration of ligands about the metal atom and facial geometry of the complexes. Our recent work on metal nitrosyl carbonyl complexes with "fac-M(CO)₅" fragment with M = Cr, Mo and W reveals that only molybdenum complex exhibits three v(C=O) bands and the corresponding chromium and tungsten analogues exhibit two v(C=O) bands. Among the group VIB metal carbonyls, molybdenum carbonyl complexes with facial arrangement exhibit IR spectra different from other two metal carbonyl complexes with facial arrangement.

In order to understand the possible transformation from facial to meridional in complex 3, we carried out a systematic synthesis. This has been done by preparing the complex 3 by dissolving NIC in various solvents to observe the changes in the IR spectral pattern. It had been observed that there is considerable influence of the solvents on the kinetics and mechanism of the reactions especially in isomerization processes and also this modifies the reaction pathways and parameters. The observed IR data of complex 3 prepared in various solvents are as follows: (i) in methanol, 1903s; 1802s; 1766s v(C=O), 1700m v(C=O); (ii) in n-propanol, 1902s; 1802sh; 1766s v(C=O), 1714m v(C=O); (iii) in isobutanol, 1902s; 1804s; 1765s v(C=O), 1700m v(C=O); and (iv) in acetone, 1902s; 1803s; 1765s v(C=O), 1707 s v(C=O). It indicates that even with solvents of different polarity and donating ability, complex 3 exhibits similar IR spectral data. This consistency in the IR spectra reveals that the solvents have no influence on the geometry of complex 3 or it is negligible. The facial geometry of the complex precursors were retained throughout the reaction and in the complexes 3 and 4 as well.

The FAB-mass spectrum of the molybdenum carbonyl complex 3 was recorded. The base peak at mass number 154 can be assigned to a (Mo + 2 CO)⁺. ²⁶Mo], the mass number at 124 can be assigned to (Mo + CO)⁺, 460 to (Mo + 3 NIC)⁺. These fragments indicate that the coordination of three molecules of NIC at the metal centre. Other fragments suggest that the composition of the complex is Mo(CO)₅(NIC). Thermogravimetric analyses (TGA) of complexes 3 and 4 were studied under N₂ atmosphere in the temperature region 50 to 800°C at a heating rate of 20°C min⁻¹. Both the complexes decompose at two different temperature regions. Molybdenum complex 3 show weight loss in the region 50-350°C and 350-800°C. Whereas tungsten analogue 4 shows weight loss at 50-140°C and 140-400°C. The major weight loss occurred at 170°C for complex 3 and 200°C for complex 4. These temperatures correspond to the decomposition of coordinated NIC ligands and the weight loss was found to be equal to the loss of three NIC ligands. This observation is in accordance with the analytical data.

Another major weight loss occurs at 460°C in complex 3 corresponding to the decomposition of molybdenum carbonate to molybdenum oxide. At 110°C complex 4 lost three coordinated CO molecules. In complex 3 weight loss corresponding to the coordinated CO was not observed which is attributed to the simultaneous formation of molybdenum carbonate. In complex 4 the M-C bond strength and the thermal energy necessary for breaking that bond is comparatively high and also the ease of formation of its carbonate derivative is low. In case small amounts of tungsten carbonates are formed and decomposed to its oxide, it is not observed in this temperature range. In complex 4, the possible doubts about the weight loss in the 50-140°C region corresponding to the loss of coordinated acetonitrile ligands is ruled out based on IR spectra.

The EGA profiles for the complexes 3 and 4 are given in Fig. 1. In complex 3, CO evolution appeared as a prominent peak at 150°C. This implies that CO was expelled from the complex at this temperature and may be present in the symmetric arrangement. There is a predominant CO evolution at 150°C and small quantity at 250°C in complex 4. This is attributed to the difference in thermal energy associated with CO evolution in complex 4 and complex 3. There is no considerable change in the CO₂ EGA profile in both the complexes. It is observed that the cleavage of CO alone from any simple organic compounds by thermal analysis is very difficult. Therefore, the possibility of evolution of CO from NIC is less and the decarboxylation is facile.
Structure of the complexes

Complexes 3 and 4 are highly air and moisture sensitive and they instantaneously decompose in solution. The powder XRD of the complexes 3 and 4 are recorded. The X-ray diffractogram of the two complexes exhibits similar pattern with considerable alignment in the relative intensities of the peaks and the d-spacing values. XRD patterns are found to be different from the free ligand NIC\textsuperscript{34}. The close matching of the observed pattern for 3 and 4 suggests facial geometry.

During the synthesis of the complexes there is a gradual colour change from the complex precursors (1, 2) to the title complexes (3, 4). This observation is an indication of the step-wise knock-out of the three coordinated CH\textsubscript{2}CN groups one by one and the subsequent coordination of three NIC molecules one by one. Based on this observation and with the IR spectra, elemental analysis, thermal and powder X-ray diffraction analysis we assign the structures of the complexes 3 and 4 shown in structure 1 (where M = Mo, W; 3, 4; and L = NIC).

Two new metal carbonyl complexes 3 and 4 with NIC as ligands were synthesized and characterized. The coordination of NIC to the metal and carbonyl stretching vibrations were studied and the discrepancies in the IR bands in the CO region were resolved. The differences exhibited by the molybdenum complex and its tungsten analogue in the IR and thermal analysis are attributed to the variation in periodic properties. Effect of solvents on the synthesis of complex 3 suggests that there is no change in the stoichiometry of the complex. The powder XRD patterns of 3 and 4 are similar suggesting same geometry.

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References