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CRITICAL REVIEWS: SPECTROSCOPIC STUDIES ON PALLADIUM (II)–COMPLEXES WITH XANTHINE AND ITS DERIVATIVES AT NORMAL AND HIGH EXTERNAL PRESSURE

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ABSTRACT

A critical reviews on molecular spectroscopic work on the palladium (II) complexes with xanthine, caffeine, theobromine, and theophyline at normal and high external pressure is presented. The methods for high external pressure measurement with the aid of Diamond Anvil Cell and Raman Measurements are also reported.

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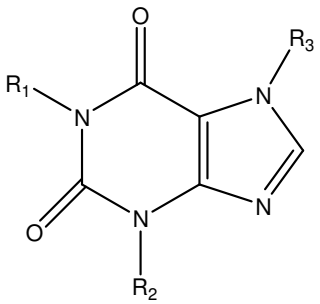
Part –I: SPECTROSCOPIC STUDIES ON PALLADIUM (II) - COMPLEXES WITH XANTHINE AND ITS DERIVATIVES AT NORMAL PRESSURE

Xanthines are a group of purine alkaloids including caffeine, theophylline and theobromine [1]. Xanthine is a product on the pathway of purine degradation and an important component of DNA, RNA and coenzymes [2}. Xanthine and its derivatives are used in the treatment of asthama, chronic bronchitis and emphysema. Caffeine is a strong stimulant and effects on the central nervous system, heart and kidney. Theobromine is a major constituent of cocoa. It has little stimulatory action on the central nervous system and it is used as a diuretic drug. Theophylline is an active constituent of tea and it is used in medicine as antiasthmatic and diuretic. Natural and synthetic xanthine derivatives have a number of bio-medical applications [3-11]. Metal ions play an important role for the transfer of ATP in biological systems [12]. The binding of metal ions to the biomolecules is of interest because of its importance in DNA replication and the inhibition of neoplastic growth [13, 14]. Recently much attention has been paid to palladium-containing complexes, due to their potent antitumor activities [15, 16]. Metal complexes of xanthine and its derivatives are also of interest because these ligands can serve as models for biologically important analogues [17, 18]. Xanthine generally bound to the metal at N-1, N-3, N-7, N-9, C-8, O-2 and O-6 positions. Xanthine coordinate to the metals through carbon adjacent to the imidazole nitrogen when the nitrogen sites are blocked with substituents [19]. The presence of an alkyl group at N-3 sterically hindered coordinates at N-9 large metal ions [20]. Caffeine is coordinated with ruthenium through C-8 [21]. The most likely binding site in caffeine and theophylline were thought to be N-9 and N-7 imidazole nitrogens, while theobromine possessed N-1 and N-9 binding sites. Coordination of neutral theophylline ligand through N-9 was reported in some Rh^{2+} and Pt^{2+} complexes [22,23] and N-7, O-6 chelation was also demonstrated [24,25]. The structure of xanthine and its derivatives is shown in Figure below:



Xanthine: $R_1 = R_2 = R_3 = H$
Caffeine: $R_1 = R_2 = R_3 = CH_3$
Theobromine: $R_1 = H$, $R_2 = R_3 = CH_3$
Theophylline: $R_1 = R_2 = CH3$, $R_3 = H$

Colacio et al. (26) has reported synthesis and characterization of Pd(II) complexes with xanthine , theophylline , theobromine , 3,8- dimethylxanthine , caffeine and 1,3,8- trimethylxanthine. Palladium containing complexes have potent anti-tumer activity. Hypoxanthine , xanthine and theobromine complexes with palladium (II) and Platinum(II) were investigated by Mikulaski and coworker [27] . Complexes of type [Pd(L) (LH)Cl] (LH= hypoxanthine , xanthine or theobromine) and [Pt(L) (LH) Cl_3] (LH= Hypoxanthine and xanthine) are prepared by reflexing 2:1 molar mixtures of hypoxanthine , xanthine or theobromine and $PdCl_2$ or $PtCl_4$ in ethanol- triethyl orhtoformate. He has also discussed possible binding sites of the bidentate bridging L^- and the unidentate terminal LH. Complexes are found to have linear polymeric chain and characterized by single monoanionic L^- ligand bridging between adjacent Pd^{2+} or Pd^{4+} ions. The Pt^{4+} complexes are *trans* –octahedral involving three terminal chloro and one terminal LH ligand per platinum. Inclusion of one terminal neutral LH and one terminal chloro-ligand completes the coordination sphere in the square-planer Pd^{2+} complexes.

Salas and Coworker [28] described thermal behavior of nine new complexes of 8-ethylxanthine (8 EH) and 8-ethyl-3-methylxanthine (3 MEH) with Ni (II) , Zn (II) , Pd (II) , Ag(I) , Cd (II) , Pt (IV), and Hg (II) by using TG, DTG and DSC thermal data. Heat of dehydration and dehalogenation were calculated from the DSC curves. Palladium complexes of the type PdL_2Cl_2 (L= 8- ethyl, 8-propyl, 8-isopropyl and 8-pheny theobromine were), prepared in acid media by Colacio-Rodriguez et al. [29]. The thermal behavior of these complexes reported by TG, DTG, and DSC techniques. A proposed scheme of thermal decomposition has also been reported.
Butsch et al. [30] investigated new organomettalic complexes of type [(R R'dppz) $Pd(Me)L]^n$ (RR' dppz = derivatives of dipyrido [3,2-a: 2', 3'-C] phenazine with RR' = 11-Cl , 11,12 Cl_2, 11-CF_3, 11-NO_2, 11-NH_2, L= Cl, I- methyluracilate (n =0), pyridine, cytosine, caffeine, or 1-methylcytosine (all n = 1) were characterized and studied in detail by electrochemical and spectroscopic (NMR, UV/VIS-absorption and emission) methods. Cytotoxicity experiments on HT-29 colon carcinoma and MFC-7 breast cancer cell line show promising activities for selected compounds. EPR spectroscopy and density functional calculation reveals markedely tuneable lowest unoccupied molecular orbital(LUMO) located at the dppz ligands.

Mixed ligand complexes of Pd(II) containing N(7) coordinations , theophylline (th) and N,N – donor ligands: 2,2' –bipyridine (2,2' – bipy) and 1,10—phenantholine (1,10-phen) were prepared by Forizs and coworker [31] . The synthesized complexes were characterized by IR, ^{1}H-NMR, ^{13}C-NMR and X-ray crystallography. Single-single X-ray structure analysis showed that the [Pd $(th)_2$(2,2'- bipy)]• H_2O• (C_6H_{14})] complex crystallizes in the monoclinic system space group $C2/_C$. The preferred site of coordination of theophylline to palladium was investigated by DFT/B3LPY calculations. The palladium (II) centre has a distorted square planar configuration with Pd-N bond length of 2.018 Å for [Pd- N(2) and Pd-N(2')] and 2.005 Å for [Pd-N(7) and Pd-N(7')].

Salas – Peregrin et al. [32] reported thermal decomposition processes for 8-ethyxanthine, 8-ethyl-3-methylxanthine and the complexes formed by these purine bases with Cu (II), Ag (I), Au (III), Pd (II). These synthesized complexes were characterized and studied by TG, and X- ray diffraction. Dehydration deamination and dehalogenation energies have been calculated from DSC curves. The neutral mononuclear [M(HTT-S(8)2(dppm)] was prepared by reaction of cis- [MCl_2(dppm)] (M= Pt (II) and Pd (II), DPPM= bis (diphenylphosphenomethane) with H2TT and NaOH by Colacio et al. [33]. Homonuclear [M-(μ-TT-N(7) S(8) (dppm)]$_2$ (M=P (II) and Pd (II) was prepared either by the reaction of [M$(HTT)_2$(dppm)] with cis- [MCl_2(dppm)] and NaOH or by the di reaction of cis- [MCl_2(dppm)] with Na_2TT prepared in situ from H2TT and NaOH. Heteronuclear [(dppm) Pt (μ-TT)2 – Pd(L-L)] complexes are obtain by reaction of [Pt(HTT)$_2$(dppm)] with [$PdCl_2$(L-L)] in basic medium.(L-L = dppm and 2,2' –bipyridine) . The crystal structure of [(dppm) Pt (μ- TT)$_2$ Pd (dppm)] • 7 H_2O is reported. The complex crystallizes in the orthorhombic space group $P2_I2_I2_I$ with a = 16.560(5) Å, b = 17.063(5) Å, c = 24.428(5) Å; 2= 4 and R_1= 0.042. The structure is consist of dinuclear units having a pseudo-2-fold perpendicular to that defined by the metal atom. The two metal atoms are bridges by two μ-TT-N (7), S (8) ligands in a head of tail arrangement. The square planar coordination of the metal atoms is completed by a chelate dppm ligand.

The complexes trans-[Pd$(tph)_2Cl_2$] , tph= theophylline-7 acetic acid , *cis*- and *trans* - [Pd$(tph)_2$ (BH) Cl_2] (BH= adenine, guanine or cytosine) and trans -[Pd$(tph)_2$ (BH) Cl_2] (BH = insosine or guanosine) have been synthesized by Vijayanthimala and Coworker [34] . These synthesized complexes were characterized by elemental and thermal analysis, electronic, IR, ^{1}H and ^{13}C NMR spectroscopic studies. They have also demonstrated coordination through the imidazole nitrogen N -9 and in some cases addition coordination through the acetate oxygen. The complexes with the theophylline-7- acetate anion. The N-9 of tph is indicated to be the most probable bonding site by extended

Huckel Molecular Orbital calculations on theophylline and structurally related xanthines. The complexes cis- [Pd (tph) (cyth) Cl_2] are found to have marginal anticancer activity.

Lusty et al. [35] has synthesized platinum metals Pt (II), Rh (II) and Pd (II) complexes with methylxanthine ligands 1-methyl, 3-methyl, 7-methyl-8-methyl and 9-mathylxanthine. The synthesized complexes were characterized by IR, ESCA, and thermal analysis. The coordination through the ring nitrogen and the oxocyclic oxygen O (2) and O (6) are also demonstrated. Palladium (II) and Platinum (II) complexes of the type $PdLX_2$, PdL_2X_2, PtL_2X_2 and the Pt (IV) complexes $PtLX_2Y_2$, $PtL_2X_2Y'_2$ (L= mono or bidentate organic ligand containing nitrogen donor atoms X = Cl or Br; Y = Br, Y' = OH) have been synthesized by Umapathy et al. [36].

Pneumatikakis [37] isolated 1:1 comlexes K [$McfCl_3$] in DMF and characterized by various physicochemical methods. The same complexes in aqueous solution are found to be unstable and decomposes to metallic palladium and platinum. The complexes are stabilized in the presence of nucleosides with the formation of mixed ligand complexes, [Mcf NuCl Cl_2](M = Metal(Pd and Pt) ,cf = caffeine, NuCl = Adenosine, Guanosine, or Inosine) and [Mcf (NuCl – H^+)Cl], (NuCl = Guanosine or Inosine) . Mixed ligand complexes were also characterized by physicochemical methods. Binding of [(COD)M(R)] 14 VE fragment (COD = 1,5- cyclooctadiene) , (R= Pd or Pt) to the nucleobases (cytosine or uracil) to the methylated nucleobases derivatives (1- methylcytosine, or t-methyluracil) and to the related ligand caffeine was investigated by Butsch and coworker [38]. From the potentially bridging cytosinate ligand a binuclear platuinum complex [(COD)(Me) Pt (N-3- cytosinate-Nt) (Pt(Me) (COD)]$^+$ was isolated. These complexes were characterized by ^1H, ^{13}C, ^{195}Pt NMR and crystal structure analysis. Relative ligand-metal bond strength is dissociated in view of ^1H-^{195}Pt NMR coupling constants.

Landaeta et al. [39] described new imidazolium salts derived from the neutral methylated xanthenes theophylline , theobromine and caffeine namely 1,3-dimethyl-9-benzulxanthinium bromide (tphBzBr) ,**Ia**) ; 3,7-dimethyl-9-benzulxanthiniumbromide(tBr2BzBr,**2a**) and 1,3,7 trimethyl-9-benzulxanthinium bromide (Caff Bz Br) ,**3a**). Some studies related to coordination chemistry of ligands **1a**-**3a** towards palladium and theoretical aspects of theophylline, theobromine and caffeine was also done. This result prove that the theophylline derivatives has thermodynamic tendency to form N-bonded species even when a equilibrium between the Pd-NHC and the "theophyllinate " was observed spectroscopically due to anisotropy NHC ligand. The solid state structure of new theophyllinate species [Pd Br_2 (tPhBz-H)$_2$(**4**)] derived from **1a**, was determined by X-ray diffraction for the confirmation of N-coordination. The analog with theobromine ligand (**2a**) coordinate palladium via N, in an analogs manner to **1a** and a mixture of the *cis /trans* isomers of its palladium complex is obtained, on the other hand , since there is no possibility of coordination in **3a** , this caffeine derivatives form a Pd-NHC compound after deprotonation with a strong base.
The mixed ligand coordination compounds of the general formula [$PdCl_2$] and [$PdLCl_2$] where L= ligand viz., uracil, uracil-4-carboxylic acid and 4-aminouracil are isolated by Srivastava et al. [40]. All synthesized compounds are found to have square planar stereochemistry around the metal ions. The synthesized compounds are synthesized elemental analysis, electrical conductance, magnetic measurements, molecular weight determination ESR, IR, and NMR studies. All synthesized compounds are found to soluble DMF, DMSO has d^8 configuration and antitumor activity.

Moreno-Vida and Coworker [41] prepared salts $(LH)_2$ [$PdBr_4$] (L= theobromine and theophylline) and $(LH)_2$ [Pd_2Br_6] (L= caffeine and various 1,3-dimethyl-8-alkylxanthines) by reactions of $PdBr_2$ in aqueous HBr. These salts are found to be strongly acidic and to dissociate in to the neutral ligands in DMSO solution. The infrared spectra are found to be consistent with the presence of mono protonated xanthinium cations and $[PdBr_4]^{2-}$ or $[Pd_2Br_6]^{2-}$ ions in all cases. Crystals of (1,3,8 - -trimethylxanthinium)$_2$[Pd_2Br_6] belong to monoclinic $P2_1/C$ space group , with a= 11.343(2) , b = 7.237(1), C= 18.647(4) Å, β= 104.26(1)^O and Z= 4 . The unit cell consists of dinuclear $[Pd_2Br_6]^{2-}$ anions containing two bridging bromide ligands, and 1,3,8 - trimethylxanthinium cations in which hydrogen are found to both imidazolic nitrogen atoms . The unit cell contain stacks of trimethylxanthine cation pairs attemating with $[Pd_2Br_6]^{2-}$ anions whereas water molecules from hydrogen bonds with partner in different stacks.
The bis-NHC palladium catalyst was prepared from caffeine by Luo et al. [42] The air and moisture stable Pd catalyst is a good catalyst in running Suzuki-Miyaura ; Mizoroki Heck and Sonogashira gaseous reactions in aqueous medium. Kaikake et al. [43] synthesized some alkyl substituted theophylline derivatives and used in extraction of metals. It is found to be high selective for palladium over other precious metals. The extraction of palladium from acid chloride media has been investigated using theophylline derivatives as extracts. Palladium (II) is found to be extracted with 7-octyltheophylline. The stoichiometric relation in the extraction of palladium was supported by mass

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spectrometry. The interaction of palladium cation anion-anion compounds ($C_4H_{10}NO)_2$ $[PdCl_4]$, $K_2[PdCl_4]$ and $K_2[PdBr_4]$ with DNA in 0.005 M and 0.15 M solutions were investigated by Kas'yaneuka and coworker [44]. These interactions were also studied by circular dichroism , viscositymetry spectrophotometry , dynamic fringence and atomic force microscopy. The palladium acido complexes and products of interactions are found to be independent of the nature of halogen in $[PdX_4]^{2-}$. The intra and intermolecular cross – linking induced palladium caused significant changes in the confirmation of DNA and palladium compounds affected by coordination of donor atoms of DNA with palladium.

Several 8-(thio) – theobromine(8-TTH_2), 8-(benzulthio) – theobromine(8- BzTTH) and 8-(methylthio) – theobromine(8-MTTH) were synthesized by Romerosa et al. [45]. These synthesized complexes were studied by IR and multinuclear (^1H, ^{31}P, ^{13}C NMR) spectroscopy in order to examine their coordination chemistry. In the complex [cis- Pd(8-BzTT)$_2$(PPH_3)$_2$]has square planar coordination about the palladium occurs through two deprotonated N7 purine atoms *cis* to each other, and two triphenylphosphine phosphorous atoms. A new organic ligand 8-(benzylthio) –theophylline (8-BzTTH) based on molecular skelton of 8-thio purine is synthesized and characterized . A new procedure to obtain 8-(methylthio)theophylline (8 -MTTH) are also investigated. Rosemerosa et al. [46] described synthesis and molecular structure of first metal complex of an analogue of guanine with Pd (II) – C (8) binding. The N (7) of guanine is the site preferred by most metal species. Present study focus on purine -metal ion interactions. They are succeeded in obtaining from an N (7) Pd (II) precursors a C (8) – Pd (II) purine complexes. The structure of C (8) – Pd (II) purine complexes has special significance because it is synthesized first time and also because of the presence of purine acidic proton.

Romerosa et al. [47] synthesized new purine derivatives S S- bis -8-(thio) –theophylline (8- $BTTH_2$) and 8-phenylthiotheophylline (8- PhTTH)$_2$ and characterized by elemental analysis , mass and standard spectroscopic measurement. The binuclear palladium (II) complex [Pd (PPh_3) (μ-Cl) (8-TT)]$_2$ (8- $BTTH_2$= 8-thiotheophylline) are synthesized by reaction of 8- $BTTH_2$ with cis – [$PdCl_2$ (PPh_3)$_2$]. In this reaction PPh_3 induced cleavage of the S-S. The complex reacts with pyridine to give a different dimeric palladium complex. [Pd (μ- S, N-8-TT) (PPh_3)Py]$_2$ in which each of the 8-thio –(theophylline) anion bind two metals through N 7 and S atoms. Reviews on structure, reactivity and biomedical applications of palladium (II) complexes in cancer therapy was described by Caires [48]. Review is focus on chemical structures of palladecycle compounds and their biological activities. Synthesis of palladium (II) complexes containing ligands derivatives of pyridines and amines in *trans* position having high antitumorial activities. The interaction of metallic complexes with biological molecules, like protein and peptides, throught terminal amine groups, carboxylate groups , imidazole group of histidine and mostly with thiol group of methionine . Some of these interactions are related to drug nefrotoxicity effect. Moreno-Vida and coworker [49] investigated bromocomplexes of Pd(II) alkylxanthine derivatives of general formula $PdBr_2(LH)_2$ and $[PdBr_4][LH_2]_2$ or $[PdBr_3][LH_2]$• x H_2O. Thermal behavior of these complexes are determined from their TG, DTG and DSC curve.

Tewari et. al. [50] has given an overview of recent molecular spectroscopic work on the methyl-xanthine alkaloid theobromine and its two closely related derivatives, caffeine and theophylline . The role of molecular spectroscopy in studies of the coordination chemistry of these methylxanthine compound is also discussed. A Renishaw in Via Raman Spectrometer equipped with argon(514 nm) laser , a charge coupled detector , 2400 lines /mm diffraction grating and an edge filter was used to measure the Raman spectra. The sample were mounted on xyz manual stage of a Leica DMLM microscope and the laser beam was focused on to the samples through a 20 x. The Raman spectrometer was calibrated prior to the measurement against the 520.5 nm Si-Si line of a silicon wafer. The spectra were recorded using 10 % Laser power and slit width of 65 μm. Several scanes were co-added to improve the signal –to- noise ratio. The acquisition time was 10 s and acquisition repeated 5 times (5 acc). All the Raman spectra were generated using the Renishaw WIRE 2.0 software (WIRE 2.0 (2002) Service Pack 6 , Renishaw plc, New Mills , Walton – under-Edge , Gloucestershire GL 12 8JR , UK) . The band positions are considered to be accurate to at least ± 1 cm^{-1}.

PART –II: SPECTROSCOPIC STUDIES ON PALLADIUM (II) - COMPLEXES WITH XANTHINE AND ITS DERIVATIVES AT HIGHER EXTERNAL PRESSURE

Xanthine is a purine found in caffeine , theobromine and theophylline and encountered in tea coffee and colas. It is a group of alkaloid that are commonly used for their effect as mild stimulants and as bronchodilators. Purine and its derivatives are biologically important components of nucleic acids (DNA, RNA) and coenzymes. It is used in

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treatment of asthma, chronic bronchitis and emphysema. Xanthine and its derivatives have several biochemical applications [51-54]. Palladium and its complexes with biologically important ligands are effectively used in cancer therapy [55-57] , cytotoxicity as well as antivirus agents[58-62], dental casting alloys [63] , antimicrobial[64] , DNA binding [65-67] and antitumer agents [68-72]. Palladium (II) complexes are also well known for its role in biological systems [73-78]. Spectroscopic studies at high external pressure is of interest because normal atmospheric pressure can not give all details in chemical reactions or catalytic cycle. Intermediate states are generally short lived and unstable at atmospheric pressure and therefore can not be detected. The application of pressure stabilizes some of these intermediate states and enabling spectroscopic measurements. A short chemical literature on high pressure spectroscopic studies on inorganic and organometallic compounds are summarized below:

Wu and coworker [79] has described the structural stability of ilmenite and Lithium niobate types of manganese titanate MnTiO3 at high pressure by x-ray diffraction and Raman spectroscopy, with diamond anvil cells. In ilmenite type TiO2 octahedral become more regular with increasing pressure while in lithium niobate type, peroveskite phase structural distortion increases with pressure. Rao et al.[80] reported high pressure behavior of the compound Bi_{12} SiO_2 by using Raman spectroscopy and x- diffraction techniques. Compounds was found to be stable in the ambient pressure cubic structure upto 26 GPa. Mode Gruneissen parameters of various Raman active modes of bismuth sillenite at high pressure is discussed in the light of the pressure- induced amorphization reported in bismuth –orthosilicate and orthogermanate. A novel cell for Raman studies at hydrogen pressure up to 200 bar and at temperatures as high as 400 ^{O}C is investigated by Domenech – Ferrer and coworker[81]. The feasibility of cell in hydrogen atmosphere was confirmed by the studies of the decomposition of $NaAlH_4$ with added TiCl3 at different hydrogen pressure and the decomposition and rehydrogenation of MgH2 and LiNH2. The device is helpful in monitoring of the formation and decomposition of chemical structures under high pressure via Raman scattering. Raman spectra of bis(diphenylglyximato) complexes of platinum and nickel under high pressure was studied by Yabuuchi et al. [82].Platinum complexes are found to be more sensitive to pressure than nickel complex. The rate of increase in Raman shift with pressure were determined. The shear strees effect applied on the [Pt ($dpg)_2$] thin film was quantitatively determined by using the relationship between the Raman shift and pressure.

Hao and coworker [83] described structural behavior of the cubic (anti-c) Ca_3N_2 at high pressure and room temperature by x-ray diffraction and Raman spectroscopic techniques. The systematic behavior of → B → A phase transition observed in Ca_3N_2. Two first –order phase transformations were observed at 9.6 and 19.5 G Pa, accompanied by large volume collapses of 7 and 9 %, respectively. Two high pressure phases were identified as monoclinic (anti-B) and hexagonal (anti-A) type structures by Rietveld refinement Shephered et al. [84] reported synthesis and crystal structure of the Fe($bpac)_2$[Ag(CN)] (bpac = 2,4' – bis (pyridyl) acetylene) and characterize its spin crossover properties by variable temperature , magnetometry and massbour spectroscopy. The pressure induced transition has also been investgated by means of high pressure Raman spectroscopy using a diamond anvil cell. It is concluded from present study that it is possible to reach the thermally – inaccessible fully low spin state at room temperature by applying hydrostatic pressure to the sample.

X-ray absorption near edge structure spectroscopy (XANES) analysis provides detailed chemical and structural information on the resultant antiwear and tribofilms form on metallic surfaces. Nicholls and coworker [85] provided a review to illustrate how XANES analysis on the micro- scale can provide the information required to elucidate complex film formation mechanism and also describes use of XANES spectroscopy to such systems. Roginski et al. [86] applied high –pressure infrared absorption spectroscopic measurement of crystalline solids of dihaltetrakis (pivalato)dichromium(III) dispersed in mineral oil over the range of 700- 1800 cm^{-1} . The electronic absorption spectra of some solid have also been measured as a function of pressure for the molecules dissolved in PMMA [poly (methyl methacrylate)] . The major feature appearing in the electronic spectra is the growth in a intensity of bond lying on the low energy side of the δ- δ* excitation.

Metal complexation and organometallic chemistry in supercritical fluid as a function of pressure and temperature was described by Yonker and coworker [87]. These investigations involve high –pressure NMR and FTIR studies of organometallic compounds in fluid solutions. The application of these spectroscopic techniques to the investigations of inorganic species in supercritical fluids is described in conjuction with the mononuclear detailes reveated of fluid solution structure and metal complexation dynamics. Carrott et al. [88] reported uv-visible spectroscopic measurement of solubilities of uranium complex [UO_2 (tta) .TBP] in supercritical CO_2 $using_h$ high-pressure micro-scale fibre - optics cells at 40 ^{0}C and over the pressure range 100-325 atm. Fibre –optic system is capable of with

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standing pressure in excess of 300 atm and spectra over the entire uv-visible range (200- 900 nm) can be obtained. Hall et al. [89] applied high pressure infrared spectroscopy to study the reactivity of the transition metal complexes $[VCl_2 (PEt_3)_4]$ with gases CO, N_2 and H_2. The reversible reaction of $[VCl_2 (PEt_3)_2]_2$ and the irreversible reaction of $[Mo_2 Cl_4(Pet_3)_4]$ with CO under pressure was also studied.

Song and coworker [90] applied ion trap mass analysis of peptide bombasin, protein myoglobin and indol alkaloid reserpine and protonated caffeine. The instrument was configured to allow for the performance characterization of a rectilinear ion trap (RIT) at pressure up to 50 m torr. The mass analysis efficiency, mass resolution, isolation efficiency and collision induced dissociation efficiency were evaluated from pressure range 1 to 50 m torr. The extent of degradation of mass resolution, isolation efficiency and ion stability as function of pressure were also characterized. Emmons and coworker [91] described the use of high –pressure fourier –transform infrared absorption spectroscopy to study poly (methylacrylate) in a dimond anvil cell at pressure up to ≈ 8 G Pa. The position of the vibrational modes were measured as a function of pressure. The data were analysed to determine mode Gruneisen parameters and bond anhormonities. These data are useful in shock compression experiments.

The highly efficient Mn^{2+} -based photoluminescence (PL) materials have received considerable attention for optical studies due to their capabilities as phosphors , sensors and their piezo- and triboluminscence properties. Rodriguez – Lazcano and coworker [92] investigated the Mn^{2+} photoluminescence (PL) of $[(CH_3)_4N]_2 MnX4$ (X= Cl , Br) under high pressure (0-15 G Pa). The reported pressure induced transformation from isolated MnX_4 (Td) to exchange coupled MnX_6 (Oh) crystals. He has also observed enormous red-shift of the green emission at 520 nm as well as new red emission at 700 nm about 6GPa. The Mn^{2+} photoluminescence (PL) behavior with pressure in these highly efficient material is investigated by time resolved spectroscopy under high pressure. Insertion of carbon monoxide into metal-methyl bond of neutral and ionic methyl and chloro palladium and platinum complexes containing hemilabile phosphorous , nitrogen ligands was illustrated by Dekker and coworker [93]. The have synthesized [(PAN) MCl_2 (M= Pd(II),Pt(II)) , [(PAN) $PdCl_2$], [{(PAN)M (CH_3)}$^+Y^-$ (Y= Cl^- , BF_4^- and $SO_3CF_3^-$)] and [{(PAN)M (CH_3) (CH_3CN) }$^+Y^-$ (Y^- = BF_4^- and $SO_3CF_3^-$)] type of complexes and characterized by high pressure NMR spectroscopy and were compared with data for bpy, dpp, dppe complexes.

Zinc, cadmium and mercury cyanide complexes of molecular formula $[K_2 M (CN)_4]$ shows two high pressure first order phase transitions have been characterized using Raman spectroscopy by Adam and Coworker [94]. The first and second phase changes are found at (1.5, 8.5) (3.0, 8.0) and (4.0, 14.0) k bars for mercury cadmium and zinc, respectively. Phase second has the trigonally –distorted spinel structure at room temperature $[Rb_2 Hg (CN)]$, whilst phase third is probable of the hausmanite type (a tetragonally –distorted spinel). Ballintine et al.[95] detected an unstable Ti(III) carbonyl $[TiCl_3(CO)(PEt_3)_2]$ by high pressure infrared spectroscopy by an easily constructed , simple operated high pressure reactor and ultraviolet –visible infrared cell. The apparatus is designed for spectral studies of the interaction of transition metal complexes and small gaseous molecules in the liquid phase.

William and coworker [96] utilized surface- enhanced Raman scattering(SERS), combined with simultaneous mass spectrometric measurements to probe the reactive nature of surface species present during the reduction of NO by CO on platinum and palladium. Simultaneous SERS /MS measurements were performed during reaction of an equimolar reactant mixture at 1atm of total pressure over both metals. Both CO_2 and N_2O were formed during reaction on Pt with onset of detectable product formation correlating with depletion of adsorbed CO and NO, respectively. In contrast, CO2 was the only product detected over Palladium, with the depletion of surface oxygen suggesting that NO dissociation may be the rate limiting at high temperature (ca300 ^OC). The extent of dissociation on these surfaces is compared and contrasted with particular emphasis placed on its role on its role in determining reaction selectivity. The high pressure polymorphism of K [Au (CN)2] has been studied by Raman scattering at ambient temperature up to 25 k bar for first and second phase transition at 6.6 and 10.5 k bar respectively by Adam and coworker[97].The phase transition is of first order therefore little structural information is obtained for either of the new phases. The reported increase in Au π- CN π* is shown in a qualitative manner to manifest itself as a red shift in the absorption and fluorescence maxima.

Molnar and coworker [98] investigated a reversible high –spin to low spin transition around 11 k bar at room temperature for the polymeric spin crossover complex [Fe(pyridine)$_2$ {Ni(CN)4}] using high pressure Raman spectroscopy. He has studied pressure dependence of vibrational frequencies in the two spin -states up to 50 k bar. It was concluded from present study that vibrational entropy change associated with the spin crossover is independent

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of pressure in this pressure range. Piezo electric fluorides of the composition $BaMF_4$ (M = Mg, Zn , Mn) have been studied at high pressure in diamond anvil cell (DAC).Raman spectroscopy and single crystal x-ray diffraction by Posse et al. [99]. All three compounds crystallize in the acentric space group $Cmcz_1$ at ambient pressure. The compound does not recover in crystallinity on decomposition. A comparison of the effects of external and chemical is also presented. The first systematic Raman study of inorganic complexes M_2 $[PtCl_6]$ (M= K, Rb, Cs, Tl , NH_4) using Diamond Anvil Cell at high pressure is reported by Adam and Coworker [100].The Pressure sensitivity of the V(Pt-Cl) modes in these complexes decreases in the order $A_{1g} > E_g > T_{1g}$ and this is correlated with the nature of atom displacements. A probable phase change is observed in Tl_2 $[PtCl_6]$. Roe et al. [101] offered practical guidelines for obtaining NMR spectra either of the metals or of the samples which are subjected to conditions of high pressure. A novel Sapphire NMR tube is described which permits high resolution operation up to 2,000 psi. These two techniques are generally available as a means of characterizing organometallic compounds.

Formation constants and changes in partial molar volume (ΔV) during association were calculated for Zn^{2+}, Mn^{2+} , Al^{3+} , Ln^{3+} Th^{4+} and Hg^{2+} complexes with SCN^- at 20 ^0C by using high pressure Raman spectroscopy by Devaure and coworker [102]. He has also discussed changes in coordination numbers upon complexation. Each of the complex cyanides $[K_2 M (CN)_4]$ (M= Zn, Cd, Hg) two high pressure first order phase transition which were characterized using Raman spectroscopy at very high pressure by Adams et al. [103] . The phase changes are at 1.5 and 8.5 k bar for M = Hg ; 3.0 and 8,0 k bar for M= Cd ; 4.0 and 14.0 M= Zn .For each material phase second has the trigonally–distorted spinel structure at room temperature. In $[Rb_2 Hg (CN)_4]$, while phase third is probable of the hausmanite type (a tetragonally – distorted spinel). Adams et al. [104] investigated Raman and for infra- red frequency shifts for some complex chlorides A_2MCl_6 (A= Cs, Rb, K) at high pressure under hydrostatic conditions in a Gasketed Diamond Anvil Cell. Using compressbilities calculated from unit cell constants and lattice energies, Gruneisen parameters γ have been obtained for all observed modes where previous data exist for comparison, it is shown that use of a Diamond Anvil Cell without gasket greatly underestimates the true shift of IR modes in particular.

Romao et al. [105] has investigated high-pressure micro-Raman spectroscopic data on copper cyanide. High-pressure Raman spectroscopic and other structural studies of hydrotalcites containing intercalated dicarboxylic acid anions are discussed by Wrights et al. [106]. Palladium (II) complexes with xanthine, caffeine, theobromine and theophylline may be prepared by the procedure reported by Salas-Peregrin and coworker [107]. The high pressure measurements were performed with the aid of a Diamond Anvil Cell (DAC) purchased from High Pressure Diamond Optics , Tuscon , AZ , USA.DACs fitted with a pair of small ($\approx$ 0.6 mm cross section) type II- A diamond exhibiting minimal fluorescence. These diamonds are glued to the polished surfaces of two opposed stainless steel pistons, which can then be squeezed together by means of a pressure plate coupled to a very strong spring. Pressure up to 100 k bar (10 G Pa, 100,000 atm)can generally achieved from these DVCs. The pair of diamonds are transparent to IR and visible / near - IR laser radiation. The R_1 fluorescence line of ruby is normally used as an Raman calibrant [108-110]. The pressure in this case is measured by expression

$$P = A / B [\{1+ (\Delta \lambda / \lambda)\}^B - 1]$$

where , P is pressure (M bar); λ is wavelength of ruby R_1 line; $\Delta \lambda$ is the shift of the R_1 fluorescence band in nm. The parameter A is 19.04 and B is either 5.0 or 7.665 corresponding to non-hydrostatic or quasi-hydrostatic pressure, respectively.

The stainless-steel gasket fixed on the surface of one DAC with plastocene and sample was introduced together with few ruby chips, into the 300 µm circular hole of a stainless- steel gasket (7 mm x 7 mm x 270 µm) with the help of Nikon SMZ 1500 microscope and squeezed between the parallel faces of the diamonds of the high pressure DACs. The purpose of the gasket is to minimize any undesirable pressure gradients across the sample. The upper and lower DAC was collected by mounting the cell in a Raman spectrometer.

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