

complex) and 10.72% (for β -nitroso complex)]. The mass loss data for the second stage of decomposition correspond to the conversion of the compound to the residue Mn_2O_4 [Mass loss: Calc.: 83.37%. Found: 84.13% (α -nitroso complex) and 84.07% (β -nitroso complex)].

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Molecular Association of Platinum Acetylacetonate with Halogens

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Complexation of platinum acetylacetonate, $Pt(acac)_2$, with molecular halogens has been studied on the basis of infrared and electronic spectral measurements. Adducts of the type, $Pt(acac)_2 \cdot X_2$ ($X = Cl, Br$ or I), have been isolated in solid state and characterized. Possible geometries of these adducts have been discussed and a synergistic bonding scheme has been proposed which involves π -donation from the highest occupied MO orbital of the halogen molecule (π^*) to an empty d_{xz} or d_{yz} orbital of the platinum together with back σ -donation from a filled d_{z^2} platinum orbital to the lowest empty MO of the halogens (σ^*). The interaction of $Pt(acac)_2$ with I_2 in CCl_4 has been studied spectrophotometrically at 25° and the formation of a charge-transfer complex has been proposed with $\lambda_{CT} = 295$ nm and blue shifted iodine band at 445 nm.

MOLECULAR complexes of the donor-acceptor type have evoked considerable interest¹ during the last two decades. The unexpected stability of some of the water insoluble metal acetylacetonates has been explained partly on the basis of benzenoid structures of the chelates²⁻⁴. These chelate rings show an important test for pseudo-aromaticity by undergoing electrophillic substitution reactions with a variety of reagents²⁻¹². Recently Singh and Sahai¹³ have demonstrated that

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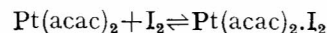
like aromatics^{14,15}, coordinatively saturated, neutral, monomeric metal acetylacetonates, $Be(acac)_2$, $Al(acac)_3$, $Sc(acac)_3$, $Zr(acac)_4$ and $Th(acac)_4$, form molecular complexes with iodine, chelate rings acting as the electron donors. The results of our studies on the molecular association of halogens with platinum acetylacetonates are reported in this note.

Platinum acetylacetonate, $Pt(acac)_2$, reacts rapidly with chlorine, bromine or iodine to form 1:1 molecular complexes, $Pt(acac)_2 \cdot X_2$ ($X = Cl, Br$ or I), in various organic solvents. The solid complexes have been isolated by mixing concentrated CCl_4 solutions of $Pt(acac)_2$ and the respective halogen in a 1:1 molar ratio at room or lower temperatures. The products precipitated rapidly and almost quantitatively from solution. The compounds readily sublime and have been characterized on the basis of elemental analysis and infrared spectra.

The infrared spectra of the solid compounds were recorded in the region $4000-250$ cm^{-1} using KBr discs. The electronic spectra were measured on a Cary 14R spectrophotometer in the region $250-700$ nm. $Pt(acac)_2$ was prepared as reported in the literature¹⁶. All the solvents used were of spectroscopic purity grade.

The infrared spectra of the three compounds, $Pt(acac)_2 \cdot X_2$, are closely similar to each other and also to that of $Pt(acac)_2$ ¹⁷, except for four bands, three in the region $1500-1000$ cm^{-1} [possibly due to $Pt(Clacac)_2$ and $Pt(acac)(Clacac)$ impurities] and one at 362 and 316 cm^{-1} exhibited by the chlorine and bromine compounds respectively. These data strongly indicate that the three halogen complexes have similar structures and that each contains an approximately planar $Pt(acac)_2$ moiety. The 316 cm^{-1} band in the bromine complex probably results from a predominantly $\nu Br-Br$ mode. Molecular complexes of Br_2 with various Lewis bases exhibit an infrared active $\nu Br-Br$ mode around 300 cm^{-1} (ref. 18). The chlorine compound does not exhibit a band around 500 cm^{-1} as expected in analogy with the bromine compound and other molecular complexes of chlorine¹⁸. However, the predominantly $\nu Cl-Cl$ mode might be masked by the $\nu Pt-O$ ¹⁷ occurring at 485 cm^{-1} . The band at 362 cm^{-1} in the chlorine complex possibly results from a predominantly $\nu Pt-Cl$ mode¹⁷. $\nu I-I$ mode was not observed but it would not be expected to lie above 250 cm^{-1} .

The interaction of molecular halogens with $Pt(acac)_2$ in solution was studied spectrophotometrically in the region $250-700$ nm. Unfortunately in the systems containing Cl_2 and Br_2 , some halogenation of the chelate rings occurs³. No such complication exists in the I_2 system. At 25° addition of I_2 to a solution of $Pt(acac)_2$ in CCl_4 [$Pt(acac)_2 = 1.0-2.5 \times 10^{-5}M$, $I_2 = 0.5 \times 10^{-5}-1.0 \times 10^{-3}M$] results in the rapid appearance of intense bands at 295 and 445 nm together with a band at 517 nm due to free I_2 . Analysis of this data shows that a 1:1 complex is formed according to the reaction:



The equilibrium constant for this reaction has been estimated to be 5.5×10^4 litres mole⁻¹. No other complexes could be detected. The $Pt(acac)_2 \cdot I_2$

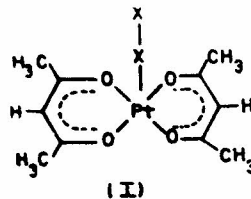
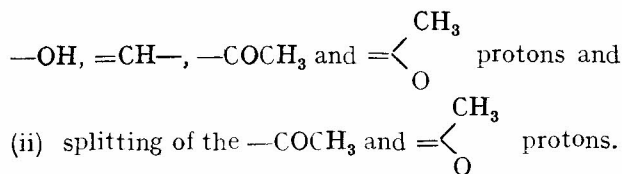
complex rapidly reacts with excess Et_3N to give $\text{Et}_3\text{N}\cdot\text{I}_2$ and with Bu_4N to give the I_3^- ion in CCl_4 . All these data indicate that the iodine in the $\text{Pt}(\text{acac})_2\cdot\text{I}_2$ complex is present in the molecular (I_2) form.

The electronic spectrum of $\text{Pt}(\text{acac})_2\cdot\text{I}_2$ in CCl_4 shows bands at 295, 325 (*sh*), 360 (*sh*) and 445 nm with ϵ_{max} values of 40600, 9890, 6250 and 12500 litres mole⁻¹ cm⁻¹ respectively. The solid state spectrum (nujol) shows bands at 292, 343 (*sh*) and 476 nm. The most interesting bands of the complex are the two high intensity bands at 295 and 445 nm. The oscillator strengths† of both the bands are very high ($f_{295} = 0.665$ and $f_{445} = 0.155$) which indicates that they result from strongly allowed transitions. The 295 nm band is probably due to a charge-transfer transition of a non-bonded platinum electron to the lowest empty MO of iodine. The band at 445 nm may be due to the blue shift of the locally excited I_2 band present at 517 nm (in CCl_4). The large magnitude of the oscillator strength ($f_{445} = 0.155$) and the heat of formation ($-\Delta H = 5.66$ kcal/mole)‡ are both consistent with the appreciable stability of the $\text{Pt}(\text{acac})_2\cdot\text{I}_2$ complex.

The interaction of halogens with $\text{Pt}(\text{acac})_2$ is probably not of the same type as reported by us¹³ in the case of some other metal acetylacetonates and iodine. In the first place the stability of the $\text{Pt}(\text{acac})_2\cdot\text{I}_2$ complex is about 20 times greater than those of the most stable complexes of iodine reported earlier¹³. Moreover, the charge-transfer bands of $\text{M}(\text{acac})_n\cdot\text{I}_2$ ($\text{M}=\text{Pt}$), complexes all lie in the narrow range of 350-370 nm¹³. These transitions are distinctly different from the higher energy transition in the case of $\text{Pt}(\text{acac})_2\cdot\text{I}_2$ at 295 nm.

It may be proposed that $\text{Pt}(\text{acac})_2$ chelate rings do not act as electron donors in the present compounds which may instead have structures of the type (I) in which a linear Pt-X-X arrangement coincides with the principal axis of $\text{Pt}(\text{acac})_2$ molecule. This is corroborated by the fact that the $\nu_{\text{Br}-\text{Br}}$ band in $\text{Pt}(\text{acac})_2\cdot\text{Br}_2$ occurs at 316 cm⁻¹ which is identical with $\nu_{\text{Br}-\text{Br}}$ of free bromine. This strongly suggests that Br_2 and possibly Cl_2 and I_2 also bond to platinum by synergistic bonding. A plausible bonding scheme involves π -donation from the highest occupied MO of the halogen molecule (π^*) to an empty d_{xz} or d_{yz} orbital of the platinum together with back σ -donation from a filled d_{z^2} Pt orbital to the lowest empty MO of the halogen (σ^*).

A detailed spectral study of acetylacetonate- I_2 system in CCl_4 is in progress. Preliminary conductometric and electronic spectral measurements of this system have indicated charge-transfer interaction between iodine and acetylacetonate but the site of charge-transfer has not yet been absolutely settled. A saturated solution of iodine in acetylacetonate (0.4M in CCl_4) gave the NMR spectrum which is almost similar to the spectrum of acetylacetonate except (i) low field shift in signals due to



These observations have recently been interpreted²⁰ in terms of charge-transfer from the acetylacetonate ring to the antibonding σ^* -orbital of iodine. However, there is no distinct possibility of charge-transfer in the present system from ketonic oxygen atoms because no effect on $\nu_{\text{C}=\text{O}}$ mode was noticed. We also investigated the $\text{Pd}(\text{acac})_2\cdot\text{I}_2$ system which would have probably behaved as the platinum system if the iodine was bonded to chelate ring (s). However, no interaction was detected between $\text{Pd}(\text{acac})_2$ and I_2 in CCl_4 .

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†The oscillator strengths have been calculated from the approximate equation, $f = 4.318 \times 10^{-9} \epsilon_{\text{max}} \Delta\nu^{1/2}$.

‡The heat formation ($-\Delta H$) of the complex was calculated from the blue shifted iodine band ($\lambda_{\text{max}} = 445$ nm) using Ham approximation¹⁹.