

refluxed in benzene and product isolated as in (b), yield 3.8 g (80% of theory) [Found: Ti, 10.60; C, 64.68; H, 4.40. $\{[(C_{10}H_9O_2)_2Ti(OC_6H_{11})]_2O$ requires Ti, 10.10; C, 65.05; H, 4.50%]. The compound is soluble in benzene.

(d) *Reaction between dicyclohexanoxo dichlorotitanium and benzoylacetone* — Dicyclohexanoxo dichlorotitanium⁸ (3.17 g; 0.01 mole) and benzoylacetone (4.05 g; 0.025 mole) were mixed in benzene (50 ml) and dry ammonia bubbled in the cold for several minutes. The precipitated ammonium chloride was filtered off, the filtrate evaporated under reduced pressure, washed with hexane and dried *in vacuo* at 60°; yield 3.8 g (80% of theory). The compound was found identical with the product obtained in (c). Other compounds were prepared similarly and were found to be identical with the products obtained from cyclohexyl titanate and the ligand.

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4-Aminoantipyrene Complexes of Fe(II)

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4 - Amino - 2,3 - dimethyl - 1 - phenyl - 5 - pyrazolone (4-aminoantipyrene, L) complexes of Fe(II) having the compositions $Fe(ClO_4)_2 \cdot 6L$, $FeCl_2 \cdot 2L$, $FeBr_2 \cdot 2L$ and $FeI_2 \cdot 2L$ have been prepared and their IR spectra, magnetic susceptibilities and conductance behaviour investigated. IR spectra show the unidentate bonding behaviour of the ligand through its carbonyl oxygen atom. All the complexes are of the high-spin type. The perchlorate complex behaves as a 1:2 electrolyte in nitrobenzene and methanol. The halo complexes behave as non-conductors in nitrobenzene but dissociate considerably in methanol. The magnetic susceptibilities along with the electronic spectra suggest a regular octahedral structure for the perchlorate complex and distorted octahedral structures for the halo complexes.

THE donor properties of 2,3-dimethyl-1-phenyl-5-pyrazolone (antipyrene) have been extensively investigated¹⁻⁴. Its 4-amino derivative also has been used as a ligand⁵. Unlike antipyrene, 4-aminoantipyrene has two potential donor sites in amino nitrogen and carbonyl oxygen. We report here the preparation and physicochemical properties of some new complexes of 4-aminoantipyrene with Fe(II) perchlorate, chloride, bromide and iodide.

Hydrated Fe(II) halides were prepared by dissolving iron powder in solutions of the respective hydrogen halides, and crystallizing the salts from the aqueous solution. Fe(II) perchlorate was prepared by dissolving iron powder in perchloric acid. 4-Aminoantipyrene was a BDH reagent of LR grade. All the solvents used were purified by standard methods⁶. The Fe(II) salt solutions were shaken with iron powder and filtered in nitrogen atmosphere before using them for the preparation of the complexes.

$Fe(L)_2Cl_2$ was prepared by mixing ethanolic solutions of $FeCl_2 \cdot 6H_2O$ (1.5 g) and the ligand (8.5 g) and evaporating the resulting solution to a syrupy mass. The mass was washed with benzene to remove excess ligand and the residue dissolved in the minimum amount of ethanol. The solution was concentrated by passing nitrogen when pale brown crystals were formed. These were washed with benzene and dried in a current of nitrogen. $Fe(L)_2I_2$ and $Fe(L)_6(ClO_4)_2$ were prepared as above. $Fe(L)_2Br_2$ precipitated when ethanolic solutions of $FeBr_2 \cdot 2H_2O$ and 4-aminoantipyrene were mixed and concentrated. The crystals were washed with ethanol followed by benzene and then dried. All the operations were carried out in an atmosphere of nitrogen. Dry solid complexes are quite stable towards aerial oxidation.

Iron in the perchlorate complex was estimated gravimetrically as Fe_2O_3 after decomposing the complex with conc. HNO_3 . Iron in the other complexes was estimated gravimetrically as Fe_2O_3 after igniting the complexes in air. Perchlorate was determined by Kurz's method⁷. The halides were estimated by Volhard's method. The analytical results are given in Table 1.

IR spectra of the ligand and the complexes (nujol mull) in the region 600-4000 cm^{-1} were recorded on a Perkin-Elmer infrared spectrophotometer model 257.

TABLE 1 — COLOUR AND ANALYTICAL DATA OF Fe(II) COMPLEXES

Complex*	Colour	Found (Calc.)	
		Metal %	Anion %
$Fe(L)_6(ClO_4)_2$	Deep brown	3.81 (3.79)	4.73 (4.81)
$Fe(L)_2Cl_2$	Yellowish	10.74 (10.47)	13.13 (13.29)
$Fe(L)_2Br_2$	Brown	8.89 (8.98)	25.61 (25.68)
$Fe(L)_2I_2$	do	7.87 (7.80)	35.29 (35.44)

*L = 4-aminoantipyrene.

The spectra in the region 200-600 cm^{-1} were obtained on a Beckman spectrophotometer model 12. Conductance measurements were carried out on a Systronics direct reading conductivity meter using a dip type cell having a cell constant of 0.571 cm^{-1} . Magnetic susceptibilities of the complexes were determined by Gouy method using $\text{Hg}[\text{Co}(\text{CNS})_4]$ as the calibrant. The electronic spectra of the complexes in the solid state were recorded using mull technique on a Unicam SP 700A recording spectrophotometer.

The molar conductance values of the perchlorate complex in nitrobenzene and methanol are 48.97 and 190.1 $\text{ohm}^{-1} \text{cm}^2 \text{mole}^{-1}$ respectively indicating it to be a 1:2 electrolyte³. The chloro, bromo and iodo complexes behave as non-electrolytes in nitrobenzene showing Λ_M of 8.29, 13.09 and 12.86 $\text{ohm}^{-1} \text{cm}^2 \text{mole}^{-1}$ respectively. However, in methanol the conductance values of the halo complexes are in the range 123.7-152.9 $\text{ohm}^{-1} \text{cm}^2 \text{mole}^{-1}$. This shows that the halo complexes dissociate considerably in a coordinating solvent like methanol.

A comparison of the IR spectral bands of the free ligand and the complexes shows that the IR frequencies of the amino group do not undergo any appreciable change on complexation. On the other hand the carbonyl stretching frequency observed at 1635 cm^{-1} in the free ligand is shifted to 1600 cm^{-1} in the spectra of complexes. This indicates that carbonyl oxygen acts as a donor atom in the complexes and that the amino group is not involved in bonding. A medium to strong intensity band appearing in the range 470-480 cm^{-1} in the spectra of the complexes and absent in the ligand spectrum can be attributed tentatively to the metal-oxygen stretching frequency⁹. Similarly, a band observed in the region 310-320 cm^{-1} for the halo complexes can be assigned to the metal-halogen stretching frequency. In the perchlorate complex ν_3 and ν_4 of the perchlorate group appear as strong bands at 625 and 1090 cm^{-1} respectively indicating the ionic nature of the perchlorate.

Since the complexes are only sparingly soluble in common solvents, the electronic spectra were recorded in the solid state. The spectra of all the complexes appear to contain an intense band below 400 nm as evidenced by the sharp decrease in the absorption above this wavelength. This may be attributed to a charge-transfer process. Though the solid state electronic spectra do not show any well defined band between 750 and 1400 nm, all the complexes show a comparatively weak absorption maximum in the range 1150-1250 nm. This can be attributed to the weak $d-d$ transition expected around 1000 nm for octahedral complexes of Fe(II).

The effective magnetic moment values show that all the complexes are of the spin-free type. The perchlorate complex shows a magnetic moment of 5.7 BM which is much higher than the spin only value of 4.9 BM. This is not surprising in view of the fact that this complex is likely to have a regular octahedral configuration as suggested by the molecular formula. A large orbital contribution to the magnetic moments is expected for a regular octahedral complex of high spin Fe(II)¹⁰. The magnetic moments of the other complexes (5.17-5.34 BM) are

in the ranges expected for tetrahedral or distorted octahedral complexes of Fe(II)^{10,11}. However the electronic spectral data supports a distorted octahedral structure for the halo complexes.

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Addition Compounds of Uranyl Chloride, Bromide & Nitrate with Diphenyl Sulphoxide, Thianthrene-5-oxide, 2,9-Dimethyl-1,10-phenanthroline & 6,6'-Dimethyl-2,2'-bipyridyl

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Addition compounds of uranyl chloride, bromide, and nitrate with diphenyl sulphoxide, thianthrene-5-oxide, 2,9-dimethyl-1,10-phenanthroline, and 6,6'-dimethyl-2,2'-bipyridyl have been prepared. IR data of the complexes are discussed and an attempt has been made to explain the type of coordinate bond formed. Diphenyl sulphide, diphenyl sulphone, and thianthrene do not form addition compounds.

A FEW complexes of uranyl chloride, bromide and nitrate with organic ligands have been prepared¹⁻³ although a large number of the complexes of uranium(IV) halides are reported in the literature³⁻⁸. The preparation and characterization of addition compounds of the uranyl salts with the title ligands are reported in this note. The addition compounds formed are similar to those reported with uranium tetrahalides.

All solvents were dried carefully by conventional methods⁹. Wherever necessary reactions were carried out under N_2 atmosphere. Uranium chlorine and bromine were determined by volumetric method