

of metal complexes ( $\log K_1$ ) were obtained from the  $\bar{n}$  versus  $pL$  curves and treated by the same methods. The values  $\Delta F^\circ$  of chelation were obtained by the temperature variation of stability constants (Table 1).

The ligand calcon (I) has three dissociable protons. The proton of the  $-\text{SO}_3\text{H}$  group was assumed to be completely dissociated under the experimental conditions as no detectable lowering of the meter reading was observed when the ligand was added to the perchloric acid solution. The values of  $\log pK_1^H$  and  $\log pK_2^H$  at  $30^\circ$  are 11.28 and 8.23 respectively. The latter value is due to the dissociation of  $-\text{OH}$  group meta to the sulphonic acid group<sup>13</sup>.

The maximum value of  $\bar{n}$  was 0.95 at an apparent  $pH$  6.5 which approximately is the hydrolysis region of the rare-earth metal ion. Regions above this value were not employed for calculations. Below this value it may hence be inferred that a 1:1 metal chelate of calcon with rare-earth metal ion is formed by bonds between metal ion and the oxygen of the *o*-hydroxy group as well as the azo group; which is evident from the analogous chelates<sup>14,15</sup>. The values of  $\log K_1$ , the stability constant for formation of a 1:1 chelate, refined by the methods outlined above, show trend similar to that observed earlier.

A linear graph between  $\log K_1$  and  $Z^2/r^{3+}$  ( $r$  is the radius of the metal ion) for various rare earth metals shows that the metal-calcon bond is essentially ionic in character<sup>16</sup>.

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## N-Benzoyl-N-phenylhydroxylamine & Cyclohexanol Derivatives of Ti(IV)\*

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N-Benzoyl-N-phenylhydroxylamine forms chelates with titanium tetrachloride and isopropyl titanate with the elimination of hydrogen chloride and isopropanol respectively. The isopropoxy derivative reacts further with bidentate ligands like salicylaldehyde, acetylacetone, benzoylacetone, dibenzoylmethane and 8-hydroxyquinoline. Similarly cyclohexanol derivatives of titanium chelates are obtained from cyclohexyl titanate or dichlorodicyclohexanoxytitanium and chelating ligands. Infrared spectra of these compounds have been studied and their molecular weights determined.

N-BENZOYL N-phenylhydroxylamine (LH) and its analogues are widely used as analytical reagents<sup>1-5</sup> in spectrophotometric and gravimetric estimation of metals. Its use in the extraction of metals<sup>5</sup> is attributed to the formation of stable chelates, and to its selective complexing properties. Nesmeyanov<sup>6</sup> was the first to report the preparation of cyclohexyl titanate; some more cyclohexyl derivatives are briefly described in literature<sup>7,8</sup>. Our interest in the study of titanium chelates led us to prepare Ti(IV) complexes of LH and cyclohexanol.

Two chloro-derivatives,  $\text{TiCl}_3(\text{L})$  and  $\text{TiCl}_2(\text{L})_2$  were prepared from the reaction of the ligand with titanium tetrachloride. As expected, the ligand replaced both the alkoxy groups of *bis*-(salicylaldehyde)diisopropoxytitanium giving *bis*-(L)*bis*-(salicylaldehyde)titanium. When reacted with isopropyl titanate, the ligand (LH), gave *bis*-(L)diisopropoxytitanium. Chelating ligands like salicylaldehyde, acetylacetone, benzoylacetone, dibenzoylmethane and 8-hydroxyquinoline replaced both the alkoxy groups of *bis*-(L)diisopropoxytitanium. (L)Trichlorotitanium also reacted with salicylaldehyde giving a mixed dichloro derivative. Ammonia was absorbed and tenaciously retained by *bis*-(L)dichlorotitanium in ether forming *bis*-(L) $\text{TiCl}_2 \cdot 4\text{NH}_3$ . The compounds prepared are listed in Table 1.

Cyclohexanoxy groups of cyclohexyl titanate were replaced by chelating ligands giving condensed complexes containing Ti-O-Ti bonds. Identical compounds were obtained when dichlorodicyclohexanoxytitanium was reacted with chelating ligands in presence of ammonia e.g., salicylaldehyde gave a product with the formula  $[(\text{C}_6\text{H}_{11}\text{O})(\text{C}_7\text{H}_5\text{O}_2)_2\text{Ti}]_2\text{O}$ . The new compounds obtained are listed in Table 2. The composition of these products was determined by elemental analysis and molecular weight determinations. The cyclohexanoxy derivatives and the ligand substituted alkoxytitanium compounds had good solubilities in boiling benzene and were found to be monomeric in the boiling solvent.

The  $\nu\text{OH}$  bands found in the free ligand at  $3105\text{ cm}^{-1}$  are completely absent in the complexes.

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TABLE 1 — N-BENZOYL-N-PHENYLHYDROXYLAMINE TITANIUM(IV) COMPOUNDS

Titanium compound (A)	Ligand (B)	Molar ratio (A: B)	Product	Colour	m.p. (°C)
TiCl <sub>4</sub>	LH	1: 2.5	(C <sub>13</sub> H <sub>10</sub> O <sub>2</sub> N) <sub>2</sub> TiCl <sub>2</sub>	Orange	180 (d)
do	do	3: 1	(C <sub>13</sub> H <sub>10</sub> O <sub>2</sub> N)TiCl <sub>3</sub>	Red	—
TiCl <sub>3</sub> (L)	do	1: 1.25	(C <sub>13</sub> H <sub>10</sub> O <sub>2</sub> N) <sub>2</sub> TiCl <sub>2</sub>	Orange	180 (d)
(SA) <sub>2</sub> Ti(OPr <sup>i</sup> ) <sub>2</sub>	do	1: 2.5	(C <sub>7</sub> H <sub>5</sub> O <sub>2</sub> ) <sub>2</sub> Ti(C <sub>13</sub> H <sub>10</sub> O <sub>2</sub> N) <sub>2</sub>	Yellow	78
Ti(OPr <sup>i</sup> ) <sub>4</sub>	do	1: 2.5	(C <sub>13</sub> H <sub>10</sub> O <sub>2</sub> N) <sub>2</sub> Ti(OC <sub>3</sub> H <sub>7</sub> ) <sub>2</sub>	do	160
TiCl <sub>3</sub> (L)	Salicylaldehyde	1: 2	(C <sub>13</sub> H <sub>10</sub> O <sub>2</sub> N)(C <sub>7</sub> H <sub>5</sub> O <sub>2</sub> )TiCl <sub>2</sub>	Brick red	—
Ti(OPr <sup>i</sup> ) <sub>2</sub> (L) <sub>2</sub>	do	1: 2.5	(C <sub>13</sub> H <sub>10</sub> O <sub>2</sub> N) <sub>2</sub> Ti(C <sub>7</sub> H <sub>5</sub> O <sub>2</sub> ) <sub>2</sub>	Yellow	78
do	Acetylacetone	1: 2.5	(C <sub>13</sub> H <sub>10</sub> O <sub>2</sub> N) <sub>2</sub> Ti(C <sub>5</sub> H <sub>7</sub> O <sub>2</sub> ) <sub>2</sub>	Brown	89
do	8-Hydroxyquinoline	1: 2.5	(C <sub>13</sub> H <sub>10</sub> O <sub>2</sub> N) <sub>2</sub> Ti(C <sub>9</sub> H <sub>6</sub> ON) <sub>2</sub>	Yellow	—
do	Dibenzoylmethane	1: 2.5	(C <sub>13</sub> H <sub>10</sub> O <sub>2</sub> N) <sub>2</sub> Ti(C <sub>15</sub> H <sub>11</sub> O <sub>2</sub> ) <sub>2</sub>	do	—
do	Benzoylacetone	1: 2.5	(C <sub>13</sub> H <sub>10</sub> O <sub>2</sub> N) <sub>2</sub> Ti(C <sub>10</sub> H <sub>8</sub> O <sub>2</sub> ) <sub>2</sub>	do	—
TiCl <sub>2</sub> (L) <sub>2</sub>	Ammonia	—	(C <sub>13</sub> H <sub>10</sub> O <sub>2</sub> N) <sub>2</sub> TiCl <sub>2</sub> ·4NH <sub>3</sub>	do	—

LH = N-benzoyl-N-phenylhydroxylamine.

TABLE 2 — CYCLOHEXANOXY TITANIUM(IV) COMPOUNDS

Reactants		Molar ratio A: B	Product
A	B		
Cyclohexyl titanate	Benzoylacetone	1: 4	[(C <sub>6</sub> H <sub>11</sub> O)(C <sub>10</sub> H <sub>8</sub> O <sub>2</sub> ) <sub>2</sub> Ti] <sub>2</sub> O
do	Dibenzoylmethane	1: 4	[(C <sub>6</sub> H <sub>11</sub> O)(C <sub>15</sub> H <sub>11</sub> O <sub>2</sub> ) <sub>2</sub> Ti] <sub>2</sub> O
Dicyclohexanoxy dichloro titanium	Benzoylacetone*	1: 2.2	[(C <sub>6</sub> H <sub>11</sub> O)(C <sub>10</sub> H <sub>8</sub> O <sub>2</sub> ) <sub>2</sub> Ti] <sub>2</sub> O
do	Dibenzoylmethane*	1: 2.2	[(C <sub>6</sub> H <sub>11</sub> O)(C <sub>15</sub> H <sub>11</sub> O <sub>2</sub> ) <sub>2</sub> Ti] <sub>2</sub> O

\*Ammonia used as HCl acceptor.

$\nu$ C=O appearing at 1630  $\text{cm}^{-1}$  in the ligand shifts to 1600  $\text{cm}^{-1}$  in the spectra of its complexes. This band may be overlapping with one of the C=C vibrations of the ligand expected in this region.  $\nu$ N—O appears in the free ligand at 920  $\text{cm}^{-1}$ . This band becomes more intense and shifts to 945  $\text{cm}^{-1}$  on complex formation  $\nu$ C=O which appears at 1635  $\text{cm}^{-1}$  in *bis*-(salicylaldehyde)diisopropoxytitanium is shifted to 1665  $\text{cm}^{-1}$  in *bis*-(L)*bis*-(salicylaldehyde)-titanium. This shift indicates a weakening of the coordination of salicylaldehyde to the metal, as expected on an increase in the coordination number of the titanium atom. The same effect is noticed in other chelates containing N-benzoyl-N-phenylhydroxylamine, dibenzoylmethane, benzoylacetone, acetylacetone and 8-hydroxyquinoline as ligands.

*Cyclohexanol complexes*—The O-H stretching vibrations of cyclohexanol are absent in its metal derivatives. The C=O stretching vibrations in dichloro-*bis*-(acetylacetonato)titanium and dichloro-*bis*-(salicylaldehyde)titanium found at 1530 and 1600  $\text{cm}^{-1}$  are shifted to 1600 and 1640  $\text{cm}^{-1}$  respectively in their chelated cyclohexanoxytitanium compounds. This indicates a weakening of the coordination of the C=O group to the metal due to the introduction of cyclohexanoxy groups. A broad band appearing between 750 and 850  $\text{cm}^{-1}$  in some of these compounds indicates the presence of a Ti-O-Ti group as shown by Fay and Lowry<sup>9</sup>.

All reactions were carried out using pure, thoroughly dried solvents and reagents in all glass apparatus fitted with permanent nitrogen flushing system. Extensive care was taken to dry nitrogen and to avoid moisture from entering the assembly. All filtrations were done under a positive pressure

of nitrogen. Molecular weights were determined by ebullioscopy in benzene in the concentration range of 0.4-1.2% w/v using a semimicro ebulliometer.

(a) *Reaction of N-benzoyl-N-phenylhydroxylamine (LH) with titanium tetrachloride*—The ligand (LH) (5.3 g; 0.025 mole) was dissolved in hexane (50 ml) containing benzene (5 ml) and titanium tetrachloride (1.1 ml; 0.01 mole) added to it. The mixture was refluxed for 2 hr to remove HCl. The orange red precipitate formed was filtered, washed with hexane and dried *in vacuo* at 60°; yield 4.9 g (90% of theory) [Found: Ti, 9.87; Cl, 13.16; C, 57.6; H, 3.98. (C<sub>13</sub>H<sub>10</sub>O<sub>2</sub>N)<sub>2</sub>TiCl<sub>2</sub> requires Ti, 9.78; Cl, 13.08; C, 57.46; H, 3.68%]. The compound is sparingly soluble in benzene, chloroform and carbon tetrachloride.

(N-Benzoyl-N-phenylhydroxylamine)trichlorotitanium was prepared similarly from the ligand (2.13 g; 0.01 mole) and titanium tetrachloride (1.65 ml; 0.015 mole); yield 3.3 g (90% of theory).

(b) *Preparation of bis-(L)diisopropoxytitanium*—A mixture of the ligand (LH) (5.32 g; 0.025 mole) and freshly distilled isopropyl titanate (2.84 g; 0.01 mole) was refluxed in benzene (50 ml) with continuous removal of the liberated alcohol. The product obtained by removing the solvent was washed with hexane and dried *in vacuo* at 60°; yield 4.7 g (80% of theory) [Found: Ti, 8.24; C, 65.01; H, 5.40. (C<sub>13</sub>H<sub>10</sub>O<sub>2</sub>N)<sub>2</sub>Ti(OC<sub>3</sub>H<sub>7</sub>)<sub>2</sub> requires Ti, 8.13; C, 65.07; H, 5.70%]. The compound is soluble in benzene and chloroform. Reactions between this product and other chelating ligands were carried out in a similar manner.

(c) *Reaction between cyclohexyl titanate and benzoylacetone*—Cyclohexyl titanate (4.44 g; 0.01 mole) and benzoylacetone (4.05 g; 0.025 mole) were

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.  $\{(C_{10}H_9O_2)_2Ti(OC_6H_{11})_2\}_2O$  requires Ti, 10.10; C, 65.05; H, 4.50%]. The compound is soluble in benzene.

(d) *Reaction between dicyclohexanoxy dichlorotitanium and benzoylacetone* — Dicyclohexanoxy dichlorotitanium<sup>8</sup> (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-Aminoantipyridine Complexes of Fe(II)

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**4 - Amino - 2,3 - dimethyl - 1 - phenyl - 5 - pyrazolone (4-aminoantipyridine, 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 (antipyridine) have been extensively investigated<sup>1-4</sup>. Its 4-amino derivative also has been used as a ligand<sup>5</sup>. Unlike antipyridine, 4-aminoantipyridine 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-aminoantipyridine 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-Aminoantipyridine was a BDH reagent of LR grade. All the solvents used were purified by standard methods<sup>6</sup>. 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-aminoantipyridine 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 method<sup>7</sup>. 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-aminoantipyridine.