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Alkoxy-boron Bridged Encapsulation Compounds of Iron(II) formed from Pentane-2,4-dione Dioxime and 1,2-Diphenylethane-1,2-dione Dioxime

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A series of alkoxy-boron bridged encapsulation compounds of iron(II) of the type $FeL_3(BX)_2$ (L = 2,4-pentanedione dioximate ion or 1,2-diphenylethane-1,2-dione dioximate ion and X = OH, OCH_3, OC_2H_5, O-i-C_3H_7 or O-n-C_4H_9) have been synthesized by adopting an in situ *procedure using iron(II) chloride, pentane-2,4-dione dioxime or 1,2-diphenylethane-1,2-dione dioxime and boric acid. The hydroxy or alkoxy groups have been derived from the solvent molecules. The compounds are all diamagnetic, well crystalline, intensely coloured (usually red or orange) and are obtained in satisfactory yields. The preparations have also been achieved in some cases by alcohol exchange trans-esterification reactions. Infrared and electronic spectra show that they are isostructural and have been presumed to possess structures between octahedral and trigonal prismatic.*

Introduction

During the past few years a number of metal complexes with novel three-dimensional 'cage like' macrocyclic ligands have been reported. These ligands, which have been derived from polycyclic crown ethers [1–5], oximes [6–20] and in a few cases with hydrazones [21], encapsulate the central metal ion and the resulting complexes exhibit interesting properties pertaining to stereochemistry, metal ion redox behaviour, analysis of metal ions and intramolecular rearrangement. Reaction of boron trifluoride etherate with bis(dimethylglyoximato)nickel(II) or tris(dimethylglyoximato)cobalt(III) yields stable complexes in which BF_2-linkages bridge the adjacent oxime groups. Apart from boron halides, other Lewis acids such as H_3BO_3, $SnCl_4$ and $SiCl_4$ have been employed for similar encapsulation reactions. Recently, a series of clathrochelates of iron(II) with dimethylglyoxime and boron compounds have been prepared *in situ* by Rose and coworkers [12, 13]. We have reported that bis(dimethylglyoximato)copper(II) and bis(acetylacetonedioximato)copper(II) complexes yield trinuclear cluster complexes with copper(II) salts having the stoicheiometries, $Cu_3(L)_2X_4$ ($X = Cl^-$ or Br^-, L = DMG or AADO) and $Cu_3L_4(NO_3)_2$ (L = DMG), through coordination of oxygen atoms of adjacent NO groups to the metal ion [22]. The nickel(II) and cobalt(II) analogues with acetylacetone dioxime have been reported [23].

Experimental

Preparation of the Complexes

Pentane-2,4-dione dioxime and 1,2-diphenylethane-1,2-dione dioxime were prepared by methods reported in literature and their melting points agreed well with the reported values [24–25]. All the compounds have been prepared under similar experimental conditions. Preparations of one alkoxy boron bridged encapsulation compound of iron(II) formed from pentane-2,4-dione dioxime and one from 1,2-diphenylethanedione dioxime are described here, as examples.

$Fe(AADO)_3(BOC_2H_5)_2$ (di-μ-ethoxyborontris(pentane-2,4-dione dioximato)iron(II)

A mixture of $FeCl_2 \cdot 4H_2O$ (1.98 g, 0.01 mol), pentane-2,4-dione dioxime (3.90 g, 0.03 mol), boric acid (1.24 g, 0.02 mol) and 40 ml of dry ethanol was stirred and refluxed for about thirty minutes whereupon the solution gradually became red and the colour rapidly deepened by slow addition of about 2.0 g of borax in small quantities during reflux. The solution thus obtained was allowed to concentrate by slow evaporation at room temperature over a period of several hours when a red crystalline product was obtained. It was filtered off, washed with small quantities of alcohol and recrystallised from acetonitrile solution. Yield was nearly 60%.

$Fe(BDO)_3(BOCH_3)_2$ (di-μ-methoxyborontris(1,2-diphenylethane-1,2-dione dioximato)iron(II)

1,2-diphenylethane-1,2-dione dioxime (7.2 g, 0.03 mol) and H_3BO_3 (1.24 g, 0.02 mol) were added to the solution of $FeCl_2 \cdot 4H_2O$ (1.98 g, 0.01 mol) in dry methanol (60 ml) and the mixture was boiled for 15 minutes when the colour of the solution

TABLE I. Principal I.r. Absorption Bands for Iron(II) Encapsulation Compounds with Pentane-2,4-dione Dioxime and Boric Acid (in cm^{-1}).[a]

H_2L	$FeL_3(BOH)_2$	$FeL_3(BOCH_3)_2$	$FeL_3(BOC_2H_5)_2$	$FeL_3(BO\text{-}i\text{-}C_3H_7)_2$	$FeL_3(BO\text{-}n\text{-}C_4H_9)_2$	Band Assignments
3380 s,b	3300 s	–	–	–	–	O–H
1600 ms	1665 m	1670 m	1668 m	1670 m	1660 m	$\mathrm{C}\underline{\cdots}\mathrm{N}$
1390 s	1450 sh	1455 sh	1485 m	1470 sh	1475 sh	(CH_3)
1320 w	1395 ms	1385 ms	1460 m	1400 m	1455 m	
	1380 m	1380 m	1395 m	1380 m	1395 m	
980 ms	1230 s	1224 s	1235 s	1230 s	1235 s	N–O
960 m	1065 s	1075 s	1070 s	1065 s	1070 s	
–	1200 s	1195 s	1195 s	1200 s	1205 s	B–O
–	1180 s	1185 s	1180 s	1175 s	1180 s	
–	800 s	775 m	765 m	770 m	775 m	

[a] s = strong; b = broad; m = medium; sh = shoulder; w = weak. L = pentane-2,4-dione dioxime ion.

changed to deep orange red and crystals having orange red colour appeared. It was filtered off after cooling, washed with methanol and recrystallised from acetonitrile. n-Butoxy, i-butoxy and i-propoxy boron compounds were prepared using the corresponding dry alcohols as media.

The compounds have also been prepared by transesterification reactions *i.e.*, by refluxing one encapsulation compound with excess of another alcohol resulting in the replacement of the OR group. Analytical data for metal, C, H and N are in agreement with the reported formulae within 0.5%.

Results and Discussion

Synthesis of the Encapsulation Compounds

The reaction taking place in the synthesis of the alkoxy boron bridged encapsulation compounds involving iron(II) chloride, pentane-2,4-dione dioxime/1,2-diphenylethane-1,2-dione dioxime and boric acid can be represented by equation 1:

$$\mathrm{Fe(II)} + 3LH_2 + 2H_3BO_3 \xrightarrow{ROH} [FeL_3(BOR)_2] + 2H^+ + 6H_2O \qquad (1)$$

where L = pentane-2,4-dione dioximate ion or 1,2-diphenylethane-1,2-dione dioximate ion

$R = H, CH_3, C_2H_5, i\text{-}C_3H_7$ or $n\text{-}C_4M_9$.

Both hydrogen ion and water which are products of the reaction besides the encapsulation compound have considerable effect on the course of the reaction. Only boric acid, without the use of borax or sodium acetate, can form the encapsulation compound but the time required is unusually long and also the yields are to some extent lower. However, when the reaction mixture is partially neutralised by gradual addition of small quantities of borax or sodium acetate or ammonium acetate (10.25–0.5 equiv/equiv of boric acid used), yields of the products are appreciably increased. The gradual deepening of the colour of the reaction solution is hastened and the time required for the solid crystals to appear is considerably reduced.

It is essential to maintain an acidic character of the reaction mixture for effective encapsulation. This has been achieved by adding controlled amounts of borax pinch by pinch, so that the progress of the reaction is hand in hand with addition of borax or sodium acetate. Rapid addition of borax or sodium acetate often results in the formation of brown products. The concentration of water has to be kept at minimum by using dry alcohol in order to prevent contamination of one encapsulation compound with another encapsulation compound which may be formed on account of transesterification reactions.

Formation of encapsulation compounds of the type $FeL_3(BX)_2$ involves a high degree of molecular organisation in which three dioxime molecules, two boric acid molecules, one iron(II) ion and two solvent molecules eventually participate. The metal ions undoubtedly play a pivotal role in the reaction process by binding the dioxime moieties in an anticonfiguration and place the oxygen atoms of the oxime groups in suitable geometrical positions for reaction with the boron containing molecules. The novel reaction processes are comparable with the molecular reorganisation in corrin type macrocyclic metal complexes [26, 27].

Infrared Spectra

In order to elucidate the structural problems infrared absorption spectra of the encapsulation compounds have been examined along with the ligands.

TABLE II. Principal I.r. Absorption Bands for Iron(II) Encapsulation Compounds with 1,2-Diphenylethane-1,2-dione Dioxime and Boric Acid (in cm^{-1}).[a]

H_2L	$FeL_3(BOH)_2$	$FeL_3(BOCH_3)_2$	$FeL_3(BOC_2H_5)_2$	$FeL_3(BO\text{-}i\text{-}C_3H_7)_2$	$FeL_3(BO\text{-}n\text{-}C_4H_9)_2$	Band Assignments
3290 s	3280 s	–	–	–	–	O–H
1590 w	1585 w	1580 w	1585 w	1590 w	1585 w	C=C of phenyl ring vibrations
1510 m	1520 m	1525 m	1530 s	1520 m	1525 m	
1440 m	1460 m	1455 m	1450 m	1460 m	1455 m	
1410 sh	1400 m	1400 m	1410 m	1415 m	1410 m	
1400 s	1505 s	1515 m	1515 s	1510 s	1510 s	C$\underline{\cdots}$N
995 s	1240 s	1235 s	1238 s	1240 s	1235 s	N–O
930 s	1090 s	1095 s	1080 s	1095 s	1090 s	
–	1185 s	1190 s	1185 s	1180 s	1195 s	B–O
–	1000 s	1005 s	1000 s	1015 s	1010 s	
–	790 m	795 m	795 m	785 m	780 m	

[a] s = strong; m = medium; sh = shoulder; w = weak. L = 1,2-diphenylethane-1,2-dione dioximate ion.

Structurally important vibrational bands are recorded in Tables I and II.

Some striking resemblances and differences between the spectra of the free ligand *i.e.*, 1,2-diphenylethane-2,4-dione dioxime and its iron(II) encapsulation compounds have been observed with regard to sharpness, intensity and position of important vibrational bands such as $\nu C\underline{\cdots}N$, $\nu N\underline{\cdots}O$, νB—O and $\nu C\underline{\cdots}C$ (phenyl) which provide valuable information for the elucidation of the structures. However, it is significant to note that there is an overall similarity between the spectra of all encapsulation compounds with minor variations arising from CH_2 or CH_3 deformation vibrations which lead us to believe that the encapsulation compounds possess similar structures.

In the region 1600–1450 cm^{-1} in the spectra of 1,2-diphenylethanedione dioxime as well as its encapsulation compounds, there appear four bands which are precisely located at 1590, 1570, 1510 and 1450 cm^{-1} respectively and arise from and are characteristic of the phenyl ring vibrations [28]. The band appearing at 1570 cm^{-1} is weak and appears mostly as a shoulder on the first band while the remaining three bands are strong.

In the spectra of 1,2-diphenylethanedione dioxime, there appears a strong band near 1400 cm^{-1}. Examining its characteristic features, we are led to believe that this band arises from C$\underline{\cdots}$N stretching vibrations. The positions of the C$\underline{\cdots}$N band in a variety of oximes have been reported [29–33]. The appearance of this band as low as 1400 cm^{-1} is undoubtedly due to a high degree of electron delocalisation in the dioxime. In the spectra of all the encapsulation compounds, this band disappears from this position and appears as a band of medium to strong intensity in the vicinity of 1500 cm^{-1}, usually weaker in intensity than the free ligand band.

The next absorption band of structural significance is the N–O stretching vibration. A group of three bands is observed in the region 1000–850 cm^{-1} in the spectra of 1,2-diphenylethane-1,2-dione dioxime which are precisely located at 990, 930 and 875 cm^{-1}. It is striking to observe that while the middle band remains practically unaffected, the bands on either side of it are most perturbed in the spectra of metal complexes and shift to a higher frequency region precisely located at 1240 and 1095 cm^{-1} respectively, suggesting that both of these bands represent the N–O stretching vibrations.

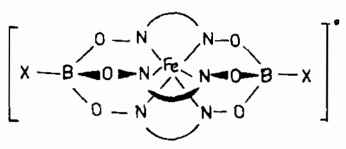
A significant feature that is observed in the spectra of the encapsulation compounds is the appearance of three new bands, similar to dimethylglyoximato and pentane-2, 4-dione dioximato iron(II) encapsulation compounds with boron compounds. These bands are absent in the spectra of the free ligand and they precisely appear in the regions 1190–1185, 1010–1000 and 790–785 cm^{-1}. We have attributed these bands to B–O stretching vibrations arising from encapsulation involving the oxygen atoms of the oxime groups and the boron atom of the boric esters. The position of these bands virtually remains the same upon substitution on the boron atom. Rose *et al.* have reported the occurrence of B–O stretching vibrational bands in the same region for the complexes of tris-glyoximatoiron(II) with boric esters.

The important features of i.r. spectra of the pentane-2,4-dione dioxime are quite complex and have been elucidated by Sahoo *et al.* Certain characteristic features of the spectra in the region 1700–1500 cm^{-1} provide evidence for the structure of the pentane-2,4-dione dioxime molecule and its encapsulation compounds.

The strong and sharp band attributed to C$\underline{\cdots}$N stretching vibration appears at 1600 cm^{-1} for pentane-2,4-dione dioxime and shifts to a higher frequency region in the spectra of the encapsulation compounds and precisely appears in the range 1660–1640 cm^{-1} with a slightly reduced intensity. A group of two bands is observed in the spectra of the free ligand in the region 100–900 cm^{-1} which are located at 980 and 960 cm^{-1}. These bands shift to a higher frequency region and appear in the region 1000–1015 and 1060–1100 cm^{-1} respectively and are assigned to N–O stretching vibrations. The shift is accounted for by coordination of the nitrogen atom of the oxime group to iron(II) ion and the oxygen atom to the boron atom of the boric esters. It is further observed that the N–O bands do not split and indicate similar vibrational energy for all the N–O groups which are symmetrically bonded to the metal ions with the nitrogen atom and boric esters with the oxygen atom.

In the spectra of the metal complexes, three additional bands which are strikingly absent in the spectra of the free ligand appear at 1180, 1000 and 785 cm^{-1} and have been assigned to the B–O stretching vibrations.

The spectral data provide a logical and selfconsistent picture to indicate the manner in which 1,2-diphenylethanedione dioxime and pentane-2,4-dione dioximate ions are coordinated with iron(II) ion and are linked with the capping agents, *i.e.* boric ester groups. The ligands are bonded to the iron(II) ion in a bidentate way through the nitrogen atoms forming five and six membered chelate rings respectively. The N–O groups are suitably disposed geometrically forming a bridge head on either side with the boric ester groups and fully encapsulate the metal ion. The electronic spectra, which are described below, are similar to dimethylglyoximato encapsulation compounds and further suggest that the structures of these molecules are similar and are postulated to be intermediate between octahedral and trigonal prismatic. The structures of the encapsulation compounds can be schematically represented as follows:



X= $-OH$, $-OCH_3$, $-OC_2H_5$, $-O-i-C_3H_7$, $-O-n-C_4H_9$

Magnetic Susceptibility and Electronic Spectra

All the encapsulation compounds are diamagnetic. The electronic spectra of the encapsulation compounds have been measured in acetonitrile in the region 10,000–30,000 cm^{-1}. The band positions are recorded in Table III. It is significant to note that no bands attributable to d–d transitions have been observed for any of the encapsulation compounds. However, all the complexes show an extremely intense band ($\epsilon \approx 15{,}000$) in the region 21,000–22,000 cm^{-1} having a half width of 3500 cm^{-1}, followed by a weak satellite band in the vicinity of 26,000 cm^{-1}. Both of these bands are presumed to be charge transfer bands arising from M–π^* transition. This assignment is based on the findings of several earlier workers on the electronic spectra of iron(II) tris(α-diimine) complexes [34]. These complexes are characterised by one or two intense bands in the visible region near 19,000 cm^{-1}. The intense bands in the electronic spectrum of $[Fe(dipy)_3]^{2+}$ have been assigned to M–π^* transition. Rose *et al.* have made similar assignments to the intense bands observed for dimethylglyoximato encapsulation compounds of iron(II) in the region 22,500–27,000 cm^{-1}. The extinction coefficients of these bands lie in the range 16,000–18,000. It is notable that the absorption bands for the present series of encapsulation compounds appear at a higher frequency region compared to the iron(II) tris(α-diimine) complexes; for example, for $[Fe(bipy)_3]^{2+}$, ν_{max} = 19,100 cm^{-1}, for $[Fe(phen)_3]^{2+}$, ν_{max} = 19,600 cm^{-1} and for $[Fe(BMI)_3]^{2+}$, ν_{max} = 17,600 cm^{-1} (where BMI = biacetylmethylimine) but at a lower frequency region as compared to dimethylglyoximato encapsulation compounds. It is also striking to note that the extinction coefficients of ν_{max} (ϵ = 14,000–16,000) have intermediate values between tris(α-diimine)iron(II) complexes (ϵ = 8000–12,000) and dimethylglyoximatoiron(II) clathrochelates.

TABLE III. Electronic Spectra of Iron(II) Encapsulation Compounds with Pentene-2,4-dione Dioxime (pddo)/1,2-Diphenylethane-1,2-dione Dioxime (deddo) and Boric Esters (cm^{-1}).[a]

Complexes	Charge Transfer Band	
	Intense and Strong	Shoulder
$Fe(pddo)_3(BOH)_2$	22,000(15,000)	27,000
$Fe(pddo)_3(HOCH_3)_2$	22,200(15,900)	26,900
$Fe(pddo)_3(BOC_2H_5)_2$	21,500(16,000)	26,100
$Fe(pddo)_3(BO\text{-}i\text{-}C_3H_7)_2$	22,000(14,300)	25,700
$Fe(pddo)_3(BO\text{-}n\text{-}C_4H_9)_2$	21,500(15,600)	25,300
$Fe(deddo)_3(BOH)_2$	21,800(14,800)	27,000
$Fe(deddo)_3(BOCH_3)_2$	21,500(14,500)	26,600
$Fe(deddo)_3(BOC_2H_5)_2$	21,900(15,800)	26,800
$Fe(deddo)_3(BO\text{-}i\text{-}C_3H_7)_2$	21,300(15,500)	26,000
$Fe(deddo)_3(BO\text{-}n\text{-}C_4H_9)_2$	21,400(15,900)	26,100

[a]The values given in the parenthesis represent extinction coefficients.

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