of the ligand is uncoordinated in these complexes. However, spectra of the P–N complexes are quite different from spectra obtained on complexes prepared with monodentate and bidentate phosphine ligands.

Discussion

The structural and magnetic properties of (bpy)Cu(DBCat) clearly are consistent with a charge distribution assignment of the metal as Cu(II) and the quinone ligand as a catecholate. The possibility of a dimeric structure for the complex had not been considered in spectral[24] and electrochemical[25] studies. In particular, it may explain the two-electron-oxidation reaction reported by Sawyer.[25] EPR spectra recorded on related complexes with phosphorus and phosphorus–nitrogen donor ligands indicate a shift in charge distribution to Cu(I)–semiquinone. The counterligand dependence of the charge distribution in the Cu–quinone chelate ring raises a question about the possibility of a $Cu^ISQ/Cu^{II}Cat$ solution equilibrium for Cu(bpy)(DBCat), similar to the cobalt and manganese examples[4,5] and the effect this might have on the chemical properties of the complex. A review of Brown's publications describing the chemical properties of the (N–N)Cu(Cat) complexes shows reactive patterns that are more common to Cu(I) species than Cu(II). Oxidation of the catechol ligand described in eq 1 occurs by O_2 attack at the metal[9] in a mechanism different from that found by Rogic for a Cu(II) system which requires oxygen for oxidation of Cu(I) in the catalytic cycle.[8] Also quite characteristic of Cu(I) is the reactivity of (bpy)Cu(DBCat) and (phen)Cu(DBCat) toward C–Cl bonds.[26] Treatment of these complexes with CCl_4 gives $(N–N)CuCl_2$ and organic products in the absence of oxygen, and the reaction is accelerated in the presence of O_2. The observation that the potassium salt of DBCat fails to react with CCl_4 points to the necessity of the Cu ion. This chemistry is similar to that of Cu(I)–phenoxide complexes and uncharacteristic of Cu(II) complexes.

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Registry No. $[Cu(bpy)(DBCat)]_2$, 103191-79-3; Cu(bpy)(DBCat)·$0.5H_2O·1.5CH_2Cl_2$, 103239-23-2; Cu(diphos)(DBSQ), 88287-15-4.

Supplementary Material Available: Tables of anisotropic thermal parameters for both structure determinations (2 pages). Ordering information is given on any current masthead page.

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Synthesis and IR, UV, NMR (^1H and ^{11}B), and Mass Spectral Studies of New β-Ketoamine Complexes of Boron: Crystal and Molecular Structure of $\overline{OC_6H_4O\underline{B}}\underline{OC(R)CHC(R')N}R''$ ($R = p\text{-}ClC_6H_4$, $R' = C_6H_5$, $R'' = CH_3$)

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Twelve new β-ketoamine complexes of boron have been synthesized and assigned tetrahedral geometry by their IR, UV, and NMR (^1H, ^{11}B) spectral and other physicochemical measurements. The mass spectrum of $\overline{OC_6H_4O\underline{B}}\underline{OC(CH_3)CHC(CH_3)N}CH_3$ is interpreted. $\overline{OC_6H_4O\underline{B}}\underline{OC(R)CHC(R')N}R''$ ($R = p\text{-}ClC_6H_4$, $R' = C_6H_5$, $R'' = CH_3$) crystallizes in the triclinic space group $P\bar{1}$ with $a = 8.577$ (4) Å, $b = 10.656$ (5) Å, $c = 11.598$ (5) Å, $\alpha = 84.77$ (4)°, $\beta = 83.25$ (4)°, $\gamma = 67.38$ (4)°, and $D_c = 1.33$ g cm^{-3} for two molecules per unit cell. The structure has been refined to $R = 0.088$ for 864 reflections. Each boron atom is bonded to one catechol and one β-ketoamine moiety. The tetrahedral environment around the boron atom is made up of two oxygen atoms from the catechol and an oxygen and a nitrogen atom from the β-ketoamine ligand.

Introduction

Examples of tetrahedral boron compounds with organic ligands such as catechol and β-ketoamines are limited in number,[2-4] and none of these have been characterized crystallographically. In our earlier studies with amino alcohol/phenol derivatives of boron,[5,6] we observe that the alkoxyboranes and 2-alkoxy-1,3,2-benzodioxaborole react with hydroxyl but not with amino protons. The derivatives $Ph_2\overline{BOCH_2CH_2N}H_2$,[7] $(p\text{-}CH_3C_6H_4)_2\overline{BOCH_2CH_2N}H_2$, and $Ph_2\overline{BOCH_2CH_2CH_2N}H_2$[8] have been shown to be tetrahedral by X-ray crystallographic studies. A detailed study of $F_2B(acac)$, $Ph_2B(acac)$, and $\overline{OC_6H_4OB}(acac)$ (acac = acetylacetonate anion) by ^1H and ^{13}C NMR spectroscopy[9,10] indicated delocalization of electrons in the β-diketonate ring, and this has been confirmed by X-ray crystal structure of $F_2B(bzac)$[11] (bzac = benzoylacetone anion) and $(OAC)_2B(acac)$[12]. The IR and ^1H NMR spectra of $\overline{OC_6H_4O\underline{B}}\underline{N(H)C(C_6H_5)CH}$-

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Table I. Physical and Analytical Data for New Boron Compounds

compd[a]	nature/color	yield,[b] %	mp, °C	anal.,[c] % B	anal.,[c] % N
Ia	buff cryst solid	80	202	4.65 (4.68)	5.86 (6.06)
Ib	yellow shiny solid	77		4.38 (4.41)	5.65 (5.72)
Ic	yellow shiny solid	90	138	4.14 (4.17)	5.33 (5.41)
Id	yellow solid	80	118	3.93 (3.96)	5.05 (5.13)
Ie	orange foamy solid	70	144	3.35 (3.37)	4.29 (4.36)
If	yellow shiny solid	68	150	3.18 (3.22)	4.12 (4.18)
Ig	yellow cryst solid	86	218	2.99 (3.05)	3.89 (3.95)
Ih	yellow cryst solid	85	151	2.81 (2.83)	4.04 (3.84)
Ii	orange-yellow cryst solid	85	85	2.86 (2.83)	3.72 (3.66)
Ij	yellow cryst solid	85	138	2.80 (2.83)	3.54 (3.66)
Ik	orange solid	65	165	2.70 (2.72)	3.48 (3.53)
Il	yellow cryst solid	86	165	2.70 (2.78)	3.56 (3.60)

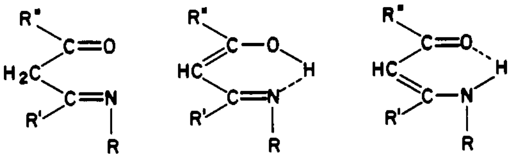
[a] All are monomeric. [b] Yield of the crystallized product. [c] Calculated values in parentheses.

$(C_6H_5)CO$ were interpreted in terms of B–N and transannular B–O bonds,[3] but this is inconsistent with our earlier observations regarding the greater reactivity of boron species with hydroxy as compared to amino groups.

In view of the above, synthesis of a new class of unsymmetrical derivatives by the reaction of 2-isopropoxy-1,3,2-benzodioxaborole with β-ketoamines is of considerable interest with regard to the nature of the bonding involved and the extent of delocalization in the unsymmetrical chelate rings.

Results and Discussion

β-Ketoamines exist in the following possible tautomeric forms:[13]



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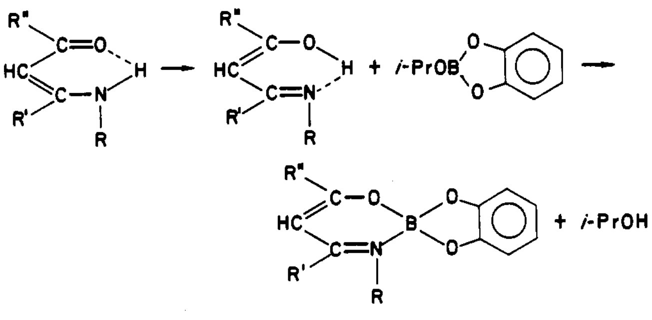
The ^1H NMR spectra indicate the presence of only the **1b** and **1c** forms in almost all the cases with a predominance of **1c**, in which the acidic protons are attached to the nitrogen atom.[14] In view of our earlier observations concerning the comparative facility of reactions of 2-isopropoxy-1,3,2-benzodioxaborole with protic reagents containing hydrogen attached to oxygen rather than the nitrogen, we thought that the reactions between 2-alkoxy-1,3,2-benzodioxaborole and β-ketoamines should occur mainly with the form **1b** and the equilibrium should gradually be shifted in the same direction, leading to the formation of boron–oxygen and transannular boron–nitrogen bonds. In order to test this hypothesis, we have investigated the general reaction



I

	R	R	R		R	R'	R"
Ia	Me	Me	Me	Ig	Me	Ph	Ph
b	Et	Me	Me	h	Et	Ph	Ph
c	*i*-Pr	Me	Me	i	*n*-Pr	Ph	Ph
d	*n*-Bu	Me	Me	j	*i*-Pr	Ph	Ph
e	*n*-Pr	Me	Ph	k	*n*-Bu	Ph	Ph
f	*n*-Bu	Me	Ph	l	Me	Ph	Ph-Cl

The completion of the mildly exothermic reaction is facilitated by the removal of liberated 2-propanol azeotropically. All the reactions were complete in 8–12 h, depending upon the nature of the β-ketoamine. Similar reactions with salicylaldimines are exothermic and are more facile. The products are soluble in benzene and can be precipitated as colored solids by adding *n*-hexane to the solutions. The complexes can be further purified by recrystallization from a benzene/*n*-hexane mixture (Table I).

The derivatives have been assigned the tetrahedral structure (I) with B–O covalent and B–N transannular bonds on the basis of spectroscopic (IR, UV, ^1H and ^{11}B NMR, and mass) evidence and by single-crystal X-ray diffraction studies in the case of $OC_6H_4OBOC(p\text{-}ClC_6H_4)CHC(C_6H_5)NCH_3$.

The infrared spectra of these compounds show (Table II) the following features: (i) an absorption band due to hydrogen-bonded OH/NH stretching frequencies at 3900–3300 cm^{-1} was observed in the spectra of the liand but absent from the spectra of the derivatives studied herein; (ii) the vibrational modes due to ν-(C═O) were virtually absent from the spectra, thus showing the chelate nature of complexes;[3] (iii) absorption bands in the range 1380–1310 cm^{-1} characteristic of a planar boron–oxygen compound,[15] e.g., OC_6H_4OBO-*i*-Pr in the present case, were found to be missing in the spectra of boron chelates; (iv) the presence of a strong band in the region 1640–1600 cm^{-1} has been assigned to C═N stretching frequencies.[16]

The ^1H NMR spectral data of the compounds Ia–g and Ij with assignments of signals are given in Table II. In compounds Ia–d the difference of 3.20 ± 0.08 ppm between the signal positions of CH_3CO and CH protons is in agreement with the magnitude of 3.20 ± 0.11 ppm observed previously in four-coordinate boron chelates derived from β-ketoamines.[3,17] However, in boron chelates derived from acetylacetone, the difference has been found to be 3.66 ppm. The derivatives Ia–d show two signals between 2.00 and 2.50 ppm, which indicates the existence of two nonequivalent methyl groups. The methyl signals are found at higher field in boron chelates prepared from 1,3-diketones. This variation may be explained on the basis of the lower degree of delocalization in the 1-oxa-5-azapentadiene moiety resulting from the unsymmetrical nature of the ligand.

The ^{11}B chemical shift is generally dependent upon the type and number of substituents around the boron atom. For example, in the tricoordinate compound (II), ^{11}B NMR signals are generally observed in the range 19.0–27.0 ppm[18] (relative to $BF_3 \cdot O(C_2H_5)_2$). However, in tetracoordinate compounds having a BNO_3 environment, the ^{11}B signal is observed in the range 2.0–14.0 ppm.[18]

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Table II. Selected UV, IR, ^{1}H NMR, and ^{11}B NMR Spectral Data for $\overline{\mathrm{OC_6H_4OB}}\mathrm{OC(R')CHC(R'')NR}$

compd				UV (MeOH)	IR	^{1}H NMR			^{11}B NMR
	R	R′	R″	λ_{max}, nm	ν(C=N), cm^{-1}	δ[a]	A[b]	assignt	δ
Ia	Me	Me	Me	305	1636 s	6.82	4 (s)	$\overline{\mathrm{OC_6H_4OB}}$	8.50
						5.48	1 (s)	=CH–	
						3.08	3 (s)	=NMe	
						2.21	3 (s)	MeC=O	
						2.18	3 (s)	MeC=N	
Ib	Et	Me	Me	300	1608 s	1.16	5 (t)	=NEt, $J = 7.0$ Hz	7.23
						2.05	3 (s)	MeC=N	
						2.22	3 (s)	MeC=O	
						3.42	5 (q)	=NEt	
						5.46	1 (s)	=CH–	
						6.95	4 (s)	$\overline{\mathrm{OC_6H_4OB}}$	
Ic	*i*-Pr	Me	Me		1620 m	6.69	4 (s)	$\overline{\mathrm{OC_6H_4OB}}$	
						5.33	1 (s)	=CH–	
						4.40–3.70	1 (m)	=NCH	
						2.20	3 (s)	MeC=O	
						2.00	3 (s)	MeC=N	
						1.25	6 (d)	$=\mathrm{NCH}{<}^{\mathrm{Me}}_{\mathrm{Me}}$, $J = 7.0$ Hz	
Id	*n*-Bu	Me	Me	290 300	1632 s	6.93	4 (s)	$\overline{\mathrm{OC_6H_4OB}}$	
						5.62	1 (s)	=CH–	
						3.55	2 (t)	=NCH$_2$-*n*-Pr, $J = 7.0$ Hz	
						2.44	3 (s)	MeC=O	
						2.35	3 (s)	MeC=N	
						2.20–1.80	7 (m)	=NCH$_2$-*n*-Pr	
Ie	*n*-Pr	Ph	Me	250, 335	1624 m	8.30–7.50	5 (m)	PhC=O	
						7.13	4 (s)	$\overline{\mathrm{OC_6H_4OB}}$	
						6.36	1 (s)	=CH–	
						3.50	2 (t)	=NCH$_2$CH$_2$CH$_3$, $J = 7.0$ Hz	
						2.41	3 (s)	MeC=N	
						2.20–1.26	2 (m)	=NCH$_2$CH$_2$CH$_3$	
						0.87	3 (t)	=NCH$_2$CH$_2$CH$_3$, $J = 7.0$ Hz	
If	*n*-Bu	Ph	Me	225, 335	1620 s	8.30–7.35	5 (m)	PhC=O	
						6.92	4 (s)	$\overline{\mathrm{OC_6H_4OB}}$	
						6.16	1 (s)	=CH–	
						3.40	2 (t)	=NCH$_2$-*n*-Pr, $J = 7.0$ Hz	
						2.33	3 (s)	MeC=N	
						1.89–0.70	7 (m)	=NCH$_2$*n*-Pr	
Ig	Me	Ph	Ph		1610s	7.95–7.65	5 (m)	PhC=O	
						7.49–7.30	5 (m)	PhC=N	
						6.75	4 (s)	$\overline{\mathrm{OC_6H_4OB}}$	
						6.12	1 (s)	=CH–	
						3.30	3 (s)	=NMe	
Ih	Et	Ph	Ph		1600 s				
Ij	*i*-Pr	Ph	Ph		1600s	8.95–7.50	10 (m)	PhC=O + PhC=N	
						6.75	4 (s)	$\overline{\mathrm{OC_6H_4OB}}$	
						6.20	1 (s)	=CH–	

[a] Spectra determined by using the R12B spectrometer in CDCl$_3$ unless otherwise stated. [b] Relative area (multiplicities in parentheses).

The ^{11}B chemical shifts of the representative compounds (Table II) are in the range 7.23–8.85 ppm, which is consistent with the tetracoordinate geometry.[18]

The main bands in the ultraviolet spectra of β-ketoamine derivatives of boron (Table II) are observed at 360–300 nm and have been attributed to a π–π^* transition[3,19,20] in the delocalization system of the chelating ligand itself. Substitution of one or both methyl groups by phenyl groups in a β-ketoamine causes a bathochromic shift[21,22] (of ~36 nm for one phenyl group and ~50 nm for two phenyl groups) of the strongest peak. A similar trend has been noted in the UV spectra of boron chelates. The phenyl group is bathochromic because it extends the conjugated system by electron release.

Table III. Mode of Fragmentation for $\overline{\mathrm{OC_6H_4OB}}\mathrm{OC(CH_3)CHC(CH_3)NCH_3}$

m/e	rel intens, %	assignt
231	100	M$^+$ (parent ion)
216	61.1	$(\mathrm{M - Me})^+$
202	14.8	$(\mathrm{M - CHO})^+$
188	20.4	$[\mathrm{M - (Me + CO)}]^+$
174	51.9	$[\mathrm{M - (Me + CH_2{=}C{=}O)}]^+$
160	22.2	$[\mathrm{M - (Me + CH_2{=}C{=}O + CH_2)}]^+$
159	24.1	$[\mathrm{M - (Me + CH{=}C{=}O + CH_3)}]^+$
148	33.3	$[\mathrm{M - (Me + CO + C_3H_4)}]^+$
136	44.4	$(\mathrm{M - C_6H_9N})^+$
119	9.3	$(\mathrm{M - C_{13}H_{18}NO})^+$
108	44.8	$(\mathrm{M - C_6H_{10}BNO})^+$
115.5	37.7	$(\mathrm{M})^{2+}$

The mass spectral fragmentation pattern of compound Ia is summarized in Table III, and the assignments are based on a

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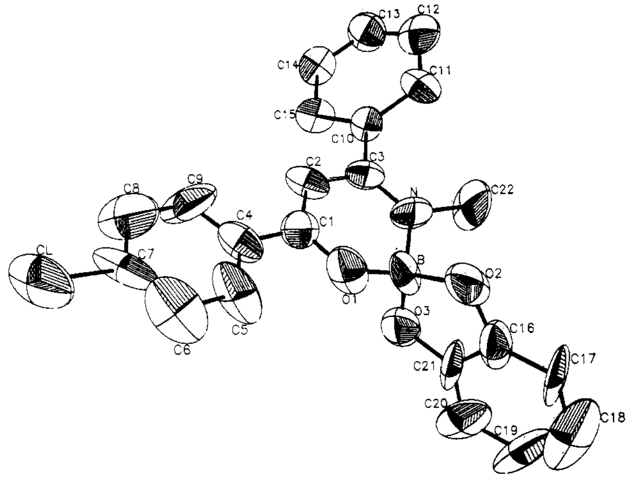


Figure 1. Structure of $\overline{OC_6H_4O}\underline{BOC(ClC_6H_4)CHC(C_6H_5)N}CH_3$.

Table IV. Bond Lengths (Å) and Angles (deg) for $\overline{OC_6H_4O}\underline{BOC(p\text{-}ClC_6H_4)CHC(C_6H_5)N}CH_3$

atoms	dist	atoms	dist
Cl–C(7)	1.78 (2)	C(2)–C(3)	1.42 (2)
O(1)–C(1)	1.33 (2)	O(1)–B	1.47 (3)
O(2)–C(16)	1.43 (3)	O(2)–B	1.46 (2)
O(3)–C(21)	1.37 (2)	O(3)–B	1.50 (3)
N–C(3)	1.32 (2)	N–B	1.56 (2)
C(1)–C(2)	1.37 (2)	N–C(22)	1.52 (2)
atoms	**angle**	**atoms**	**angle**
B–O(1)–C(1)	123 (1)	B–O(2)–C(16)	110 (2)
B–O(3)–C(21)	107 (2)	B–N–C(3)	121 (2)
B–N–C(22)	116 (2)	C(3)–N–C(22)	123 (1)
O(1)–B–O(2)	111 (2)	O(1)–B–O(3)	111 (2)
O(2)–B–O(3)	104 (2)	O(1)–B–N	110 (2)
O(2)–B–N	109 (2)	O(3)–B–N	110 (2)

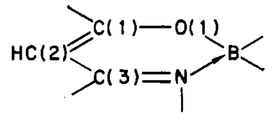
review on organoboron compounds by Cragg and Weston.[23] The assignment of the boron-containing peaks is supported by the $^{10}B/^{11}B$ isotope pattern (showing the ratio 1:4). The significant features are (i) the molecular ion peak is the base peak, which is indicative of its greater stability, (ii) nearly all the ions are boron-containing, (iii) thermodynamically unstable borenium ions are also formed, (iv) the boron–nitrogen bond appears to be stronger since a large number of fragments contain both boron and nitrogen, and (v) the fragmentation of Ia generally occurs from the parent molecular ion by the loss of radicals such as methyl or formyl, which is followed by elimination of a molecule like carbon monoxide or propyne from other fission products.

The crystal structure of a representative compound, $\overline{OC_6H_4O}\underline{BOC(p\text{-}ClC_6H_4)CHC(C_6H_5)N}CH_3$, has been determined. A molecular illustration is presented as Figure 1, and bond lengths and angles are given in Table IV. Each boron atom is bonded to one catechol and one β-ketoamine moiety. The tetrahedral environment around the boron atom is made up of three oxygen atoms (one from a β-ketoaminate ligand and two from a catecholate ligand) and one nitrogen (from a β-ketoaminate ligand). The B–O bond distances of 1.45 (2) Å, (B–O, catecholate) and 1.47 (2) Å (B–O, β-ketoaminate) are comparable to the average B–O distance of 1.46 Å found in bis(acetato)(acetylacetatonato)boron(III) and in other boron compounds having BO_3N type bonding. The B–N bond distance (1.56 (2) Å) is essentially the same as the sum of covalent radii (1.58 Å). It may, however, be noteworthy that this transannular B–N bond distance is comparable with those found in $CH_3NH_2{\cdot}BF_3$ (1.57 Å), $H_3N{\cdot}BF_3$ (1.56 Å), and cubic boron nitrile[24] (1.57 Å) but is shorter by 0.11 Å as compared to some other tetracoordinated compounds having a BO_3N skeleton such as $\overline{N(CH_2CH_2CH_2O)_3B}$ (1.67 Å)[25] and $\overline{N(CH_2CH_2O)_3B}$ (1.67 Å).[26] This shows a strong transannular B–N bond in the compound studied herein as compared to the case of boratranes[27,28] having similar environments of oxygen and nitrogen atoms. Additionally, a comparative study of the structural parameters of the compounds $Ph_2\overline{BOCH_2CH_2CH_2N}H_2$, $Ph_2\overline{BOCH_2CH_2N}Me_2$, $(CH_3C_6H_4)_2\overline{BOCH_2CH_2N}H_2$,[8] and $Ph_2\overline{BOCH_2CH_2N}H_2$[7] also reveals a stronger B–N transannular bond in the compound studied herein.

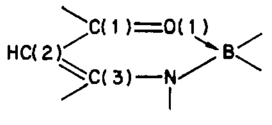
The cyclic C(3)–N bond distance (1.32 (2) Å) is comparable with that found in dimethylglyoximate complexes of nickel (1.29, 1.30 Å) and palladium (1.31 Å)[29] as well as *N,N'*-disalicylaldimine-1,2-phenylenediamino chelates of various metals[30] and with that of bis(*N-tert*-butylsalicylaldiminato)palladium.[31]

The C(1)–O(1) bond distance (1.33 (2) Å) lies between the values of single (1.43 Å) and double (1.23 Å) carbon–oxygen bond lengths, whereas the bond distances between C(1)–C(2) (1.37 (2) Å) and C(2)–C(3) (1.42 Å) lie between the theoretical C=C and C—C distances (1.33 and 1.54 Å, respectively). The exocyclic $H_3C(22)$–N (1.52 (2) Å) bond distance is slightly longer than the normal single C–N bond (calculated as 1.47 Å). A comparison of bond distances in the title compound to those in related derivatives is presented in Table V.

Out of the two plausible resonating forms, (A) and (B), in which these β-ketoamine complexes of 2-isopropoxy-1,3,2-benzodioxaborole could exist, even the limited accuracy of the present structural data for one of the complexes, $\overline{OC_6H_4O}\underline{BOC(p\text{-}ClC_6H_4)CHC(C_6H_5)N}CH_3$, suggests a larger contribution from structure A compared to that from structure B with a small amount of delocalization mainly confined over the B–O(1)–C(1)–C(2) atoms.



A



B

Experimental Section

All manipulations have been carried out under anhydrous conditions. Nitrogen was estimated by Kjeldal's method,[32] boron as methyl borate,[33] and the alkoxy group by oxidation with potassium dichromate in 12.5% sulfuric acid.[34] The 2-alkoxy-1,3,2-benzodioxaboroles were prepared by a published procedure.[5] IR spectra were recorded as Nujol mulls on a Perkin-Elmer Model 337 or 557 spectrophotometer. ^1H NMR and mass spectra were recorded on Perkin-Elmer R-12B and Hitachi RMU.6E spectrometers, respectively. UV spectra were recorded on a Toshniwal Model RL 02184 spectrophotometer.

Synthesis of 2-(β-Diketoamino)-1,3,2-benzodioxaboroles (Ia–e). Since a similar method was followed for the synthesis of all these derivatives, only one representative example is discussed here. Other details are given in Table I.

To a benzene solution (60 cm^3) of 2-isopropoxy-1,3,2-benzodioxaborole (3.32 g, 18.65 mmol) was added 4-(methylamino)-3-penten-2-one

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Table V. Comparison of B–O, C–O, and C–N Bond Distances (Å) of Tetracoordinated Boron Compounds

compd	B–O	B–N	C–N	C–O	ref
$OC_6H_4OBOC(p\text{-}ClC_6H_4)CHC(C_6H_5)NCH_3$	1.47 (β-ketoaminate)	1.56	1.32 (cyclic)	1.33	present work
	1.48 (catecholate av)		1.52 (exocyclic)		
$Ph_2BOCH_2CH_2CH_2NH_2$	1.481	1.643	1.498	1.437	8
$Ph_2BOCH_2CH_2NMe_2$	1.476	1.691	1.490	1.418	8
$(p\text{-}CH_3C_6H_4)_2BOCH_2CH_2NH_2$	1.492	1.690	1.505	1.388	8
$N(CH_2CH_2O)_3B$	1.43	1.67	1.65	1.43	27
$N(CH_2CH_2CH_2O)_3B$	1.44	1.67	1.52	1.43	25
$Ph_2BOCH_2CH_2NH_2$	1.484	1.653	1.485	1.484	7
$C_6H_5B(OCH_2CH_2)_2N$	1.460	1.666	1.483	1.411	26

Table VI. Summary of Data Collection

compd	$OC_6H_4OBOC(p\text{-}ClC_6H_4)CHC(C_6H_5)NCH_3$
mol wt	389.6
space group	$P\bar{1}$
cell consts (22 °C)	
a, Å	8.577 (4)
b, Å	10.656 (5)
c, Å	11.598 (5)
α, deg	84.77 (4)
β, deg	83.25 (4)
γ, deg	67.38 (4)
cell vol, Å^3	970.5
molecules/unit cell	2
ρ(calcd), g cm^{-3}	1.33
μ(calcd), cm^{-1}	2.24
radiation, monochromated (λ, Å)	Mo Kα (0.71069)
max cryst dimens, mm	0.20 × 0.35 × 0.83
scan width	0.80 + 0.20 tan θ
std reflcns	200, 040
decay of stds	±2%
no. of reflcns measd (*h*,±*k*,±*l*)	1876
2θ range, deg	≤40
no. of reflcns considered obsd	864
no. of params varied	288
COF (unit weights)	1.84
R	0.088
R_w	0.088

(2.11 g, 18.66 mmol). The reaction mixture was refluxed, and the 2-propanol thus liberated was fractionated azeotropically with benzene over a period of 8 h. The progress of reaction was followed by estimating the 2-propanol in the azeotrope (found, 0.72 g; calcd, 0.73 g). After completion of the reaction, excess solvent was removed under reduced pressure and the yellow solid product was recrystallized form a benzene/*n*-hexane mixture (3.52 g, 80%). Mp 202 °C. Anal. Calcd for $C_{12}H_{14}BNO_3$: B, 4.68; N. 6.06. Found: B, 4.65; N, 5.88.

X-ray Data Collection and Structure Refinement for $OC_6H_4OBOC(R)CHC(R')NR''$ (R = *p*-ClC_6H_4, R′ = C_6H_5, R″ = CH_3). An elongated plate appropriate for the X-ray study was sealed in a glass capillary. Final lattice parameters as determined from least-squares refinements of the angular settings of 15 reflections (2θ > 30°) accurately centered on an Enraf-Nonius CAD-4 diffractometer are given along with other pertinent crystallographic parameters in Table VI. Following correction for Lorentz and polarization but not for absorption effects, the structure was solved via application of the direct-methods program MULTAN.[35] Subsequent least-squares refinements were carried out with the SHELX program package.[36] Out of 1876 reflections observed, 864 data were used in the refinement. With all non-hydrogen atoms with anisotropic thermal parameters, final values of $R = [\sum(|F_o| - |F_c|)/\sum|F_o|] = 0.088$ and $R_w = [\sum w(|F_o| - |F_c|)^2/\sum F_o^2]^{1/2} = 0.088$ were obtained. The phenyl group bonded to C3 was found to exhibit a disorder about the C(3), C(10), C(13) vector. This is therefore essentially a rotational disorder about the C(3)–C(10) bond. The refinement is based on a 0.5 occupancy factor for atoms C(11), C(12), C(14), and C(15). Hydrogen atoms were not loctable. Neutral-atom scattering factors were taken from the compliations of Cromer and Mann,[37] and corrections for the real and imaginary components of anomalous dispersion were taken from the table of Cromer and Liberman.[38] Final fractional atomic coordinates are given in Table VII.

Table VII. Final Fractional Coordinates for $OC_6H_4OBOC(p\text{-}ClC_6H_4)CHC(C_6H_5)NCH_3$

atom	*x*/*a*	*y*/*b*	*z*/*c*
Cl	1.0007 (8)	0.2157 (6)	0.0486 (6)
O(1)	0.702 (2)	0.095 (1)	0.581 (1)
O(2)	0.671 (2)	0.115 (1)	0.789 (1)
O(3)	0.426 (2)	0.165 (1)	0.696 (1)
N	0.632 (2)	−0.078 (1)	0.713 (1)
B	0.610 (5)	0.075 (2)	0.692 (2)
C(1)	0.751 (2)	0.007 (2)	0.498 (2)
C(2)	0.748 (2)	−0.120 (2)	0.516 (1)
C(3)	0.692 (2)	−0.162 (1)	0.628 (1)
C(4)	0.816 (2)	0.061 (2)	0.388 (2)
C(5)	0.821 (3)	0.188 (2)	0.381 (2)
C(6)	0.868 (4)	0.243 (3)	0.277 (3)
C(7)	0.930 (2)	0.164 (3)	0.188 (3)
C(8)	0.926 (3)	0.034 (2)	0.186 (2)
C(9)	0.867 (3)	−0.020 (2)	0.292 (2)
C(10)	0.796 (2)	−0.307 (1)	0.639 (1)
C(11)	0.770 (4)	−0.389 (4)	0.741 (3)
C(12)	0.802 (4)	−0.532 (4)	0.746 (3)
C(13)	0.737 (2)	−0.581 (2)	0.653 (2)
C(14)	0.691 (4)	−0.498 (3)	0.552 (3)
C(15)	0.658 (4)	−0.355 (3)	0.545 (3)
C(11)P	0.571 (4)	−0.330 (3)	0.701 (3)
C(12)P	0.571 (5)	−0.462 (3)	0.708 (3)
C(14)P	0.836 (5)	−0.540 (4)	0.600 (4)
C(15)P	0.840 (5)	−0.410 (4)	0.584 (3)
C(16)	0.537 (4)	0.227 (2)	0.844 (2)
C(17)	0.539 (4)	0.294 (3)	0.935 (2)
C(18)	0.384 (7)	0.400 (4)	0.972 (3)
C(19)	0.243 (4)	0.424 (3)	0.912 (3)
C(20)	0.238 (3)	0.355 (2)	0.815 (2)
C(21)	0.394 (4)	0.251 (2)	0.785 (2)
C(22)	0.573 (3)	−0.120 (2)	0.833 (1)

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Registry No. Ia (CC entry), 102696-41-3; Ia (boric acid entry), 102683-02-3; Ib (CC entry), 102696-42-4; Ib (boric acid entry), 102683-03-4; Ic (CC entry), 102696-43-5; Ic (boric acid entry), 102683-04-5; Id (CC entry), 102724-19-6; Id (boric acid entry), 102696-40-2; Ie (CC entry), 102696-44-6; Ie (boric acid entry), 102683-05-6; If (CC entry), 102696-45-7; If (boric acid entry), 102683-06-7; Ig (CC entry), 102696-46-8; Ig (boric acid entry), 102683-07-8; Ih (CC entry), 102696-47-9; Ih (boric acid entry), 102683-08-9; Ii (CC entry), 102696-48-0; Ii (boric acid entry), 102683-09-0; Ij (CC entry), 102696-51-5; Ij (boric acid entry),

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102683-10-3; Ik (CC entry), 102696-49-1; Ik (boric acid entry), 102683-11-4; Il (CC entry), 102696-50-4; Il (boric acid entry), 102683-12-5; 2-isopropoxy-1,3,2-benzodioxaborole, 61676-63-9; 4-(methylamino)-3-penten-2-one, 14092-14-9; 4-(ethylamino)-3-penten-2-one, 50967-59-4; 4-(isopropylamino)-3-penten-2-one, 59487-11-5; 4-(butylamino)-3-penten-2-one, 57717-00-7; 4-(propylamino)-3-penten-2-one, 83696-44-0; 2-(butylamino)-1-propenyl phenyl ketone, 76943-80-1; 2-(methylamino)-2-phenylethenyl phenyl ketone, 891-16-7; 2-(ethylamino)-2-phenylethenyl phenyl ketone, 20964-96-9; 2-(propylamino)-2-phenylethenyl phenyl ketone, 57167-94-9; 2-(isopropylamino)-2-phenylethenyl phenyl ketone, 102683-00-1; 2-(butylamino)-2-phenylethenyl phenyl ketone, 57167-95-0; 2-(methylamino)-2-phenylethenyl 4-chlorophenyl ketone, 102683-01-2.

Supplementary Material Available: Listings of fractional coordinates, anisotropic and isotropic temperature factors, and bond lengths and bond angles (3 pages). Ordering information is given on any current masthead page.

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Organotin Intercalation Compounds of FeOCl: Synthesis, ^{57}Fe and ^{119m}Sn Mössbauer and Infrared Spectroscopy, and Powder X-ray Diffraction Studies

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Four new organotin intercalates of FeOCl were synthesized and studied by infrared and variable-temperature ^{57}Fe and ^{119m}Sn Mössbauer spectroscopies and by X-ray powder diffraction. These systems were chosen to provide a detailed microscopic spectroscopic examination of both the host and the guest species as well as a comprehensive picture of the guest–host interaction. The neat organotins, 4-$(CH_3)_3Sn(C_5H_4N)$ (P1), $(CH_3)_3SnN(CH_3)_2$ (A1), $(CH_3)_2Sn[N(CH_3)_2]_2$ (A2), and $Sn[N(CH_3)_2]_4$ (A4), all show evidence for an increase in tin coordination upon intercalation to form nominally $FeOCl(P1)_{1/7.5}$ (INP1), $FeOCl(A1)_{1/5.5}$ (INA1), $FeOCl(A2)_{1/8}$ (INA2), and $FeOCl(A4)_{1/16}$ (INA4). The intercalation process is described as a redox process where an electron is first donated to the FeOCl lattice with the corresponding formation of a pyridinium ligand for INP1 and an iminium ligand for INA1, INA2, and INA4, which then enter between the layers of the FeOCl matrix. The intercalated species in INP1 is described as an associated moiety with both four- and five-coordinate tin and an abnormally low charge transfer to the lattice, which is attributed to the large size of the guest. Data for INA1, INA2, and INA4 are interpreted in terms of six-coordinate tin species in which the fifth and sixth sites are lattice chlorines. An additional organic intercalation compound, $FeOCl[(CH_3)_2N^+{=}CH_2]_{1/5}[Cl^-]_{1/10}$, was also prepared and studied as a model compound for the intercalation of the organotin amines. ^{57}Fe Mössbauer relaxation calculations have been used to determine the extent of the charge transfer to the lattice.

Introduction

Iron oxychloride is a strongly anisotropic compound that can admit guest molecules between its layers to form a variety of intercalation compounds. The detailed structure of FeOCl was reported by Lind,[1] confirming the earlier work of Goldsztaub.[2] The unit cell parameters are $a = 378.0$, $b = 791.7$, and $c = 330.2$ pm. The orthorhombic space group is P_{mnm}. The structure consists of a corrugated (in two dimensions) iron–oxygen framework sandwiched between planes of chlorine atoms to form one layer of the lamellar material. The interlayer bonding is a weak van der Waals interaction. In the intercalation process these weak interactions are broken (except for the intercalates formed with unsolvated alkali cations) and the layers are pried apart to accommodate the guest species. When the limiting stoichiometry is reached, the resulting FeOCl intercalation compounds consist of alternating guest and host layers with each van der Waals layer expanded to its final dimension.

A number of organic, organometallic, and metallic species have been intercalated into FeOCl, including pyridine and substituted pyridines,[3] ammonia[4] and amines,[5] phosphines and phosphites,[6] alkali metals,[7] and metallocenes.[8] Although few guest structural or orientation studies have been carried out on FeOCl-containing systems, several important conclusions have been reached for the related ammonia and pyridine intercalates of TaS_2, as well as for isostructural host materals such as NbS_2 and TiS_2. Guest species that can be intercalated into FeOCl usually also form intercalation compounds in TaS_2. A plot of the interlayer expansion in FeOCl vs. the analogous parameter in TaS_2 was shown to have a strong linear correlation,[9] suggesting that the guest orientation and guest–host bonding interaction in the two hosts are similar. This allows the more comprehensive TaS_2 structural studies to be generalized to the corresponding FeOCl intercalates.

A widely accepted redox mechanism for intercalation into these matrices was proposed by Schöllhorn.[10] An electron is first donated to the lattice from a potential guest species, presumably near the surface of the lattice. This is followed by intercalation of a positively charged species, either the original product of the redox process or a more stable positively charged species formed by further reaction. A number of intercalation compounds of FeOCl and TaS_2 are formed under mild conditions, indicating that the metal host atoms in these lattices are easily reduced. In almost all cases, neutral guest species or solvents are co-intercalated and are usually thought of as solvating species for the charged guest moieties.

Previous studies in this laboratory[3,9,11,12] have used X-ray powder diffraction, ^{57}Fe Mössbauer spectroscopy, and Fourier transform infrared spectroscopy to study organic intercalates of FeOCl. In the present study a number of organotin compounds, which can participate in the Schöllhorn mechanism, have been synthesized and successfully intercalated into FeOCl. Employing organotins as guest species permits the additional use of ^{119m}Sn Mössbauer spectroscopy to elucidate the changes in the guest as well as the host moieties and serves as an additional probe of the intercalated layer system. The present study summarizes the results of both

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