Syntheses and Characterization by NMR Spectroscopy and X-ray Diffraction of Complexes Derived from Metals of Groups 2 and 13 and the Ligand Bis(3,5-di-*tert*-butyl-1-hydroxy-2-phenyl)amine

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Reaction of 3,5-di-*tert*-butylcatechol and aqueous ammonia with boron, aluminum, gallium, or strontium chloride, or with calcium or barium acetate produce, under oxidizing conditions, neutral complexes of stoichiometric formulae ML (M = BCl), ML_2, [M = Al (**2**), Ga (**3**), Ca (**4**), and Ba (**5**)], and ML_3H [M = Sr (**6**)] [L = different oxidation states of bis(3,5-di-*tert*-butyl-1-hydroxy-2-phenyl)amine]. The structures of **1** and **4**–**6** were established by ^{1}H- and ^{13}C-NMR spectroscopy and of **2**, **3**, and **6** by X-ray diffraction. The coordination compound ClBL (**1**) was obtained by transmetallation of ZnL_2 with BCl_3. It is a tetracyclic compound with tetracoordinated boron and nitrogen atoms, the ligand being in the reduced form, bis(hydroxyphenyl)amine. The paramagnetic complexes **2** and **3** crystallized in the triclinic system and are hexacoordinated with two orthogonal planar ligands bonded to the metal atoms. The ligands appear in two different oxidation states: one as the monoanion and another as a radical dianion. Based on their X-ray diffraction molecular structures, it is deduced that both ligands have similar structures, confirming electronic delocalization and fast interconversion of their oxidation states. Ca and Ba complexes are diamagnetic and hexacoordinated, both ligands being monoanions The strontium complex crystallized in the monoclinic system, the metal atom is nonacoordinated, having two ligands as monoanions, and a third one is a neutral protonated diquinone. Its structure is a distorted helix with three paddles in a C_3 geometry and its unexpected diamagnetic behaviour is due to the presence of a reduced protonated ligand.

Introduction

We are interested in developing the heterocyclic chemistry of main-group elements and bis(hydroxyphenyl)amines.[1−7] These heterocycles are particularly stable and are suitable models for structural and spectroscopic investigation. The preparation of some organometallic heterocycles bearing a bis(hydroxyphenyl)amine ligand has already been reported.[2,6,8−10] A relevant property of the bis(hydroxyphenyl)amine molecules is that they allow the stabilisation of uncommon species such as some which contain pentacoordinated phosphorus atoms.[1,2,4]

The template synthesis with 3,5-di-*tert*-butylcatechol and metals in the presence of ammonia lead to metallic hexacoordinated complexes bearing two ligands formed by the condensation of two catechol molecules to one nitrogen atom.[11] The complexes have two planar, tridentate ligands. The analogous transition-metal complexes of general formula ML_2 have been the subject of extensive research work[11−19] and several X-ray diffraction structures have been reported.[12−18] Theoretically, several different stable oxidation states could exist for this ligand, ranging in charge from 0 to -3 (Scheme 1). It is surprising that only the monoanion (**III**) and the radical dianion (**IV**) have been found in the previously reported complexes. The oxidation state of the ligand depends on the nature of the metals: With metals in oxidation state II both ligands appear as monoanion (**III**), while for metals in oxidation state III one ligand is a monoanion (**III**) and the other is a radical dianion (**IV**), and in metals in oxidation state IV both are radical dianions (**IV**).

The reports in the literature have focused on complexes formed with two different oxidation forms of the ligand, **III** and **IV**. Detailed magnetic and electrochemical studies of these compounds have been performed.[11−21] The magnetic studies indicate that there is a strong ferromagnetic coupling between the ligands through the empty metal orbitals. It was proposed that they are valence tautomers with an intramolecular electronic tautomeric equilibrium due to electronic transfer between the ligand and the metal.[21] In addition, it was found by electrochemical studies that the complexes can suffer one-electron oxidation or one-electron reduction, both processes occurring at the ligand-based orbitals.[20]

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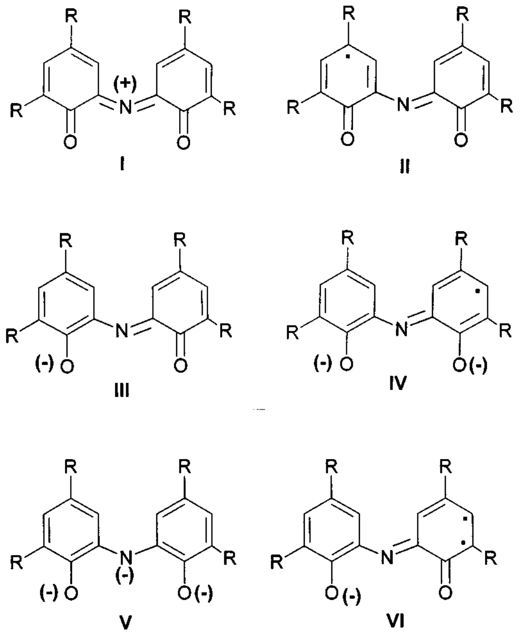


Scheme 1. Oxidation states of the bis(3,5-di-*tert*-butyl-1-hydroxy-2-phenyl)amine ligand

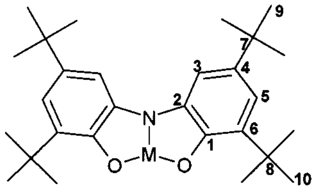
The versatile behaviour of this ligand guarantees the interest of further studies on these compounds. Relatively little effort has been directed toward synthesising and studying the reactivity of the bis(hydroxyphenyl)amines and main-group and alkaline-earth metals. Therefore we have investigated the complexes derived from bis(3,5-di-*tert*-butyl-1-hydroxy-2-phenyl)amine and boron (**1**), aluminium (**2**), gallium (**3**), calcium (**4**), barium (**5**), and strontium (**6**). During the preparation of this manuscript the synthesis and a magnetic investigation for the aluminium derivative has been reported;[21] the crystal structure for this compound is presented in this study.

Results and Discussion

Compound **1** has been synthesized by BCl_3 transmetallation of ZnL_2. Complexes **2−6** have been prepared directly by reaction of 3,5-di-*tert*-butylcatechol and the metallic chloride or acetate in the presence of ammonia. All are dark solids.

Compounds **1** and **4−6** are diamagnetic and their ^{1}H-NMR spectra are similar (Table 1). The ^{13}C-NMR spectra of the complexes **1** and **4−6** (Table 2) show six resonances in the aromatic domain indicating that the phenyl rings in each complex are equivalent. The chemical shift of atom C-1 in compound **1** is $\delta = 153.9$, characteristic of a phenoxy group. In contrast, the chemical shift for this atom in compounds **4−6** ($\delta = 176-180$) is consistent with quinone character. The chemical shift for the ^{11}B-NMR resonance ($\delta = +14.9$) of compound **1** indicates that the boron atom is tetrahedral and coordinated to the nitrogen atom. ^{1}H- and ^{13}C-NMR data, the mass spectrum and the elemental analysis indicate that the boron atom is bonded to one chlorine atom and to one reduced ligand **V**. Its structure is depicted in Scheme 2.

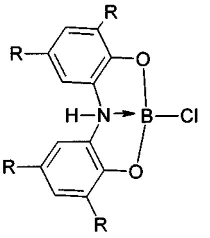
Table 1. ^{1}H-NMR chemical shift data of complexes **1** and **4−6** (in C_6D_6); the numbering of the atoms is shown in the figure



Compound	3-H	5-H	9-H (*t*Bu)	10-H (*t*Bu)
1	7.21	6.95	1.34	1.28
4	7.05	6.89	1.20	1.08
5	7.08	6.91	1.22	1.11
6	7.26	6.75	1.37	1.24

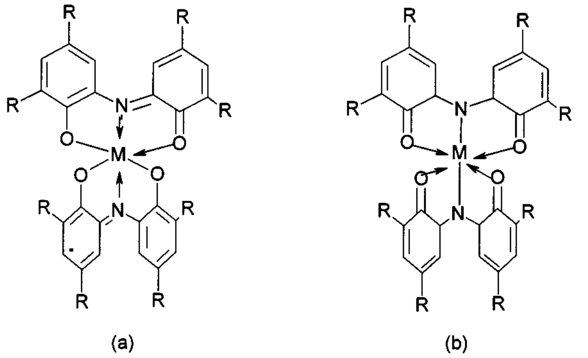
Table 2. ^{13}C-NMR chemical-shift data of complexes **1**, and **4−6** (in C_6D_6)

Compound	C-1	C-2	C-3	C-4	C-5
1	153.9	130.9	116.3	140.6	123.5
4	176.8	142.7	117.4	144.3	130.7
5	176.0	142.8	117.5	144.4	130.7
6	178.6	142.0	116.5	144.0	130.2
	C-6	C-7	C-8	C-9	C-10
1	135.3	34.6	31.7	34.4	29.2
4	142.8	35.21	30.43	34.73	29.43
5	143.5	35.1	30.3	34.7	29.5
6	142.8	34.7	29.4	34.1	28.7



Scheme 2. Proposed structure for compound **1**

Complexes **2** and **3** were found to crystallize from CH_2Cl_2/ethanol. Crystals of **2** and **3** are triclinic, space group $P-1$. Selected bond length and angles are listed in Table 3 and the molecular structures are depicted in Figures 1−3. The neutral complexes **2** and **3** show oxygen atoms occupying the equatorial sites of an octahedron, with two tridentate ligands, the four cycles of each ligand lying almost in the same plane. The MO_4N_2 coordination spheres show only slight distortions in bond angles at the equatorial atoms. Thus, angles for compound **2** are O2−Al−O4 91.0(2), O2−Al−O3 91.5(2), O1−Al−O4 92.3(2), O1−Al−O3 89.6(2)°, and those for compound **3** are O1−Ga−O4 92.7(1), O1−Ga−O3 91.5(1), O2−Ga−O4 89.8(1), O2−Ga−O3 91.52(14)°, while the angles between the atoms N−M−O show deviations from ideal octahedral geometry (Tables 3, 4). The nitrogen atoms are in *trans* positions [N1−Al−N2 176.8(3) and N1−Ga−N2 176.7(1)°]. The M−O bond lengths are identical, for compound **2** the average Al−O bond length is 1.877(5) Å and for compound **3** the average Ga−O bond length is 1.959(3) Å, similar to the Ga−O bonds reported for other hexacoordinated gallium compound [1.96(1) Å].[8] The Al−N and Ga−N bond lengths differ slightly [Al−N1 1.982(5), Al−N2 1.976(5), Ga−N1 2.014(3), Ga−N2 2.025(3) Å]. It is proposed[21] that the Al and Co^{III} compounds are formed by the bonding of two ligands in two different oxidation states, ligand **III** and ligand **IV** (Schemes 1 and 3). The C−O bond lengths in **2** and **3** are similar (1.29 Å) and indicate a double-bond character; the C−N bond lengths are also similar and their lengths are in between a double and a single bond (1.35 Å). The pattern of carbon−carbon bond lengths in **2** and **3** shows that the bonds C3−C4 and C5−C6 are consistently shorter than the other C−C bonds. We could not distinguish, based on bond lengths, two different structures of the ligands that could be attributed to different oxidation states. This could mean that the ligands become similar by the electronic delocalization and fast interconversion of the oxidation states between them as has been proposed for other compounds.[21]



Scheme 3. (a) Proposed structure for compounds **2** and **3**; (b) proposed structure for compounds **4** and **5**

From the NMR data and elemental analysis, it is deduced that compounds **4** and **5** derived from calcium and barium are bonded to two monoanionic ligands **III** in a hexacoordinated array analogous to that of aluminium and gallium complexes.

Compound **6** crystallizes from CH_2Cl_2/ethanol monoclinic in space group *P*2(1)/*c*, and its X-ray structure is shown in Figures 3−4. The complex presents a new coordination behaviour because three ligands are bonded to a metal centre, resulting in a nonacoordinate strontium atom. The nine bond lengths between the strontium and the ligands are normal coordination bonds with Sr−O bonds varying from 2.47 to 2.71 Å, whereas the Sr−N bonds vary from 2.67 to 2.77 Å. The strontium bond lengths are in accord with another nonacoordinated compound [strontium bis(thiocyanate)−hexaethylene glycol].[22] The structure of the molecule can be best described as a helix of three paddles of distorted C_3 geometry. If the different oxidation states of the ligand are considered the compound must be formed by two ligands in the monoanion oxidation state (**III**) plus a neutral radical (**II**). This description would not, however, correspond to a diamagnetic compound. Looking carefully at the X-ray diffraction structure the presence of

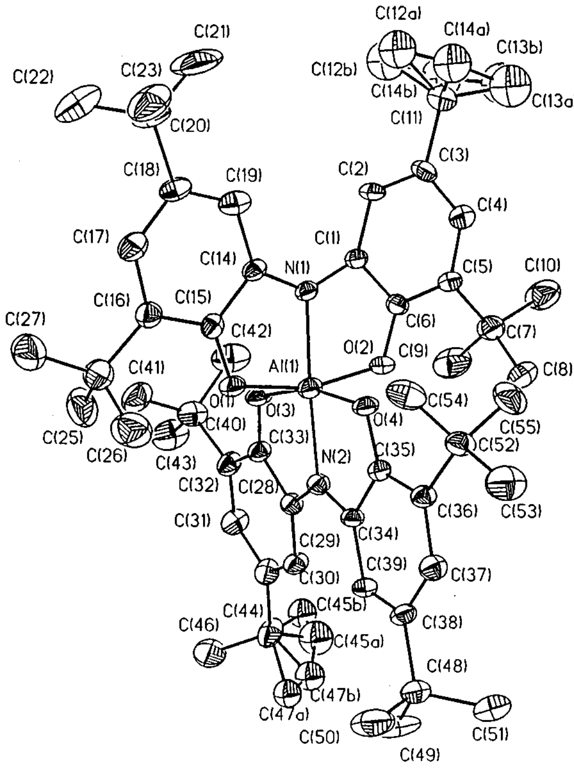


Figure 1. Molecular structure of $C_{56}H_{80}AlN_2O_4$ (**2**); thermal ellipsoids represent a 30% probability

Table 3. Selected bond lengths [Å] and angles [°] for compound **2**

Bond lengths [Å]			
Al−O1	1.874(5)	Al−O2	1.871(5)
Al−O3	1.885(5)	Al−O4	1.879(5)
Al−N1	1.981(5)	Al−N2	1.975(5)
O1−C1	1.292(7)	O2−C7	1.289(7)
O3−C13	1.288(8)	O4−C19	1.300(7)
N1−C2	1.351(8)	N1−C8	1.352(8)
N2−C20	1.345(8)	N2−C14	1.352(8)
C1−C6	1.426(9)	C1−C2	1.440(9)
C13−C18	1.427(9)	C13−C14	1.443(9)
C2−C3	1.413(9)	C3−C4	1.364(9)
C14−C15	1.419(9)	C15−C16	1.355(9)
C4−C5	1.40(1)	C5−C6	1.372(9)
C16−C17	1.42(1)	C17−C18	1.365(9)
C7−C12	1.405(9)	C7−C8	1.464(9)
C19−C24	1.419(9)	C19−C20	1.446(9)
C8−C9	1.409(9)	C9−C10	1.351(9)
C20−C21	1.415(9)	C21−C22	1.351(8)
C10−C11	1.42(1)	C11−C12	1.368(9)
C22−C23	1.424(9)	C23−C24	1.367(9)
Bond angles [°]			
O2−Al−O1	164.2(2)	O2−Al−O4	91.0(2)
O1−Al−O4	92.3(2)	O2−Al−O3	91.5(2)
O1−Al−O3	89.6(2)	O4−Al−O3	163.8(2)
O2−Al−N2	96.1(2)	O1−Al−N2	99.7(2)
O4−Al−N2	81.7(3)	O3−Al−N2	82.1(3)
O2−Al−N1	82.2(3)	O1−Al−N1	82.2(3)
O4−Al−N1	95.7(2)	O3−Al−N1	100.5(2)
N2−Al−N1	176.9(3)		

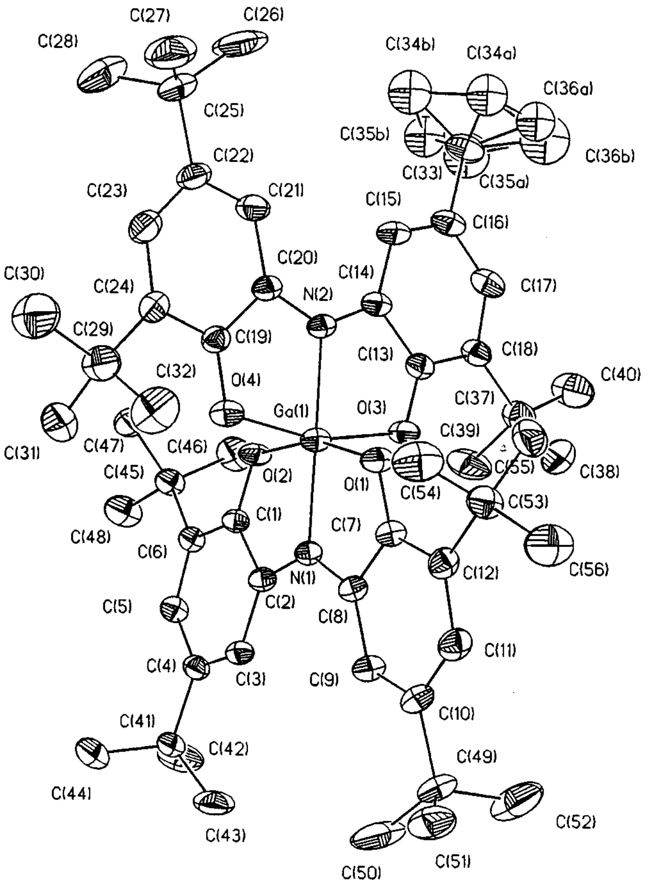
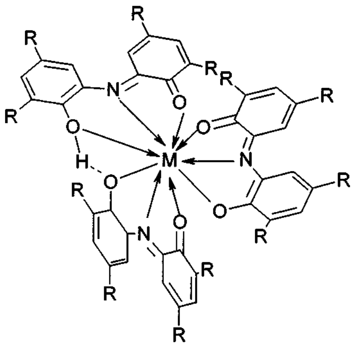


Figure 2. Molecular structure of $C_{56}H_{80}GaN_2O_4$ (**3**); thermal ellipsoids represent a 30% probability

Table 4. Selected bond lengths [Å] and angles [°] for compound **3**

Bond lengths [Å]			
Ga−O1	1.967(3)	Ga−O2	1.965(3)
Ga−O3	1.952(3)	Ga−O4	1.954(3)
Ga−N1	2.015(3)	Ga−N2	2.024(3)
O1−C7	1.294(5)	O2−C1	1.291(5)
O3−C13	1.299(5)	O4−C19	1.291(5)
N1−C2	1.351(5)	N1−C8	1.357(5)
N2−C20	1.3486)	N2−C14	1.354(6)
C1−C6	1.427(6)	C1−C2	1.4556)
C13−C18	1.4236)	C13−C14	1.456(6)
C2−C3	1.417(6)	C3−C4	1.356(6)
C14−C15	1.418(6)	C15−C16	1.360(7)
C4−C5	1.423(6)	C5−C6	1.360(6)
C16−C17	1.4107)	C17−C18	1.368(7)
C7−C12	1.431(6)	C7−C8	1.445(6)
C19−C24	1.425(7)	C19−C20	1.449(6)
C8−C9	1.410(6)	C9−C10	1.353(6)
C20−C21	1.423(6)	C21−C22	1.362(7)
C10−C11	1.424(7)	C11−C12	1.367(6)
C22−C23	1.407(7)	C23−C24	1.3657)
Bond angles [°]			
O2−Ga−O1	161.9(1)	O2−Ga−O4	92.8(1)
O1−Ga−O4	89.8(1)	O2−Ga−O3	91.5(1)
O1−Ga−O3	91.6(1)	O4−Ga−O3	162.3(1)
O2−Ga−N2	96.0(1)	O1−Ga−N2	102.1(1)
O4−Ga−N2	81.0(1)	O3−Ga−N2	81.4(1)
O2−Ga−N1	80.9(1)	O1−Ga−N1	81.0(1)
O4−Ga−N1	100.2(1)	O3−Ga−N1	97.4(1)
N2−Ga−N1	176.7(1)		

a hydrogen atom sitting between the oxygen atoms O4 and O5 was discovered (bond lengths: O4−H 1.341 Å, O5−H 1.148 Å, bond angle O4−H−O5 174.1°) and the position of this hydrogen atom was freely refined (x, y, z; H_{iso} = 0.0897). Thus, the third ligand was in fact a new reduced neutral form of the ligand (Scheme 4). In each ligand, the four carbon and nitrogen atoms are found in a plane. If only these atoms are considered the structure resembles a helix formed with three bidentate chelates in a hexacoordinated array (Figure 4). If the oxygen atoms are examined, they lie slightly out of the plane for each ligand and they are folded in a *trans* orientation. Examination of the bond lengths shows that the two ligands bonded to the hydrogen atom are similar with one short C−O bond length (1.23−1.26 Å) and a longer C−O one (1.33 Å, Table 5). The other ligand has two short C−O bonds (1.26 Å). The point group of **6** is not perfectly C_3 because of the presence of the hydrogen atom, the bond lengths of the atoms bonded to the strontium atom are different. The presence of the hydrogen bonding between atoms O4 and O5 makes the angle O4−Sr−O5 narrower [54.6(1)°] than the other two similar angles O2−Sr−O3 [90.03(1)°] and O6−Sr−O1 [87.7(1)°]. One of the ligands presents shorter distances [Sr−O1 2.475(2), Sr−O2 2.476(2) Å] than the other two [Sr−O3 2.569(2), Sr−O4 2.686(2) Å and Sr−O5 2.719(2), Sr−O6 2.575(2) Å]. The aromatic rings in each ligand are twisted due to the steric effect of the *tert*-butyl groups and the helical structure.



Scheme 4. Proposed structure for compound **6**

Conclusions

The X-ray diffraction of complexes of Al and Ga show that they are isostructural and that the ligands in these compounds also have similar structures, confirming the electronic delocalization and fast interconversion of the oxidation state of the ligands (**III** → **IV**). Hexacoordinated complexes are also proposed for the diamagnetic complexes of Ba and Ca. The strontium compound is the first example with a nonacoordinated metal atom for the complexes with bis(3,5-di-*tert*-butyl-1-hydroxy-2-phenyl)amine as ligand. The compound has three tridentate ligands in a distorted helix of three paddles, with a geometry close to C_3. The diamagnetic behaviour results from the presence of a new

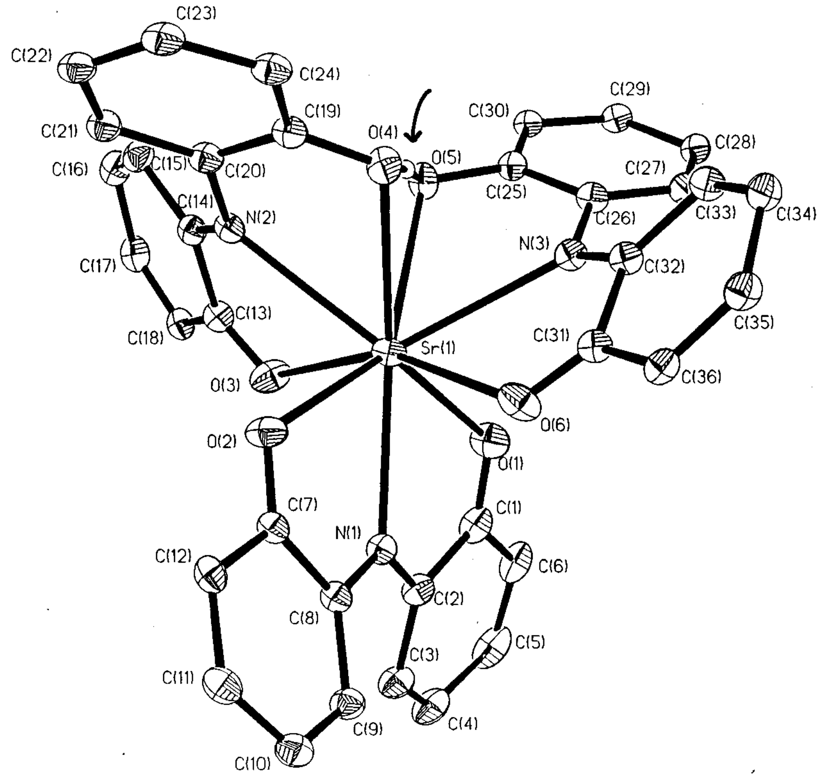


Figure 3. Molecular structure of $C_{84}H_{120}SrN_3O_6$ (**6**); the *tert*-butyl groups are not shown and the arrow marks the position of the hydrogen atom bonded to O4 and O5; thermal ellipsoids represent a 25% probability

oxidation state of the ligand that transforms the neutral radical oxidation state **II** (Scheme 1) into a diamagnetic neutral one.

Experimental Section

General Remarks: All solvents were freshly distilled and dried before use according to established procedures. − Melting points were measured with a Gallenkamp apparatus and are uncorrected. − The IR spectra were taken in KBr discs using a Perkin Elmer 16F PC IR spectrometer. − All the NMR spectra were obtained on a JEOL GXS-270 and JEOL-400 spectrometers in $CDCl_3$ solution. ^1H- and ^{13}C-NMR spectra were measured with TMS as the internal reference. − Elemental analyses were performed with a Fisons Instrument EA 1108 elemental analyzer CHNS-O. − Mass spectra were obtained with a Hewlett-Packard HP 5989A. − The X-ray

Table 5. Selected bond lengths [Å] and angles [°] for compound **6**

Bonds lengths [Å]							
Sr−O1	2.475(2)	Sr−O2	2.476(2)	Sr−O3	2.569(2)	Sr−O4	2.686(2)
Sr−O5	2.719(2)	Sr−O6	2.575(2)	Sr−N1	2.667(2)	Sr−N2	2.762(2)
Sr−N3	2.771(2)	O1−C1	1.258(4)	O2−C7	1.262(3)	O3−C13	1.231(3)
O4−C19	1.332(4)	O5−C25	1.337(3)	O6−C31	1.231(3)	N1−C2	1.342(4)
N1−C8	1.345(3)	N2−C20	1.394(3)	N2−C14	1.302(3)	N3−C26	1.397(3)
N3−C32	1.295(3)	C1−C6	1.457(4)	C1−C2	1.471(4)	C2−C3	1.434(4)
C3−C4	1.355(4)	C4−C5	1.436(5)	C5−C6	1.359(5)	C7−C8	1.466(4)
C8−C9	1.429(4)	C9−C10	1.359(4	C10−C11	1.431(4)	C11−C12	1.369(4)
C7−C12	1.450(4)	C13−C14	1.505(4)	C14−C15	1.449(4)	C15−C16	1.354(4)
C16−C17	1.455(4)	C17−C18	1.347(4)	C13−C18	1.472(4)	C19−C20	1.418(4)
C20−C21	1.406(4)	C21−C22	1.383(4)	C22−C23	1.408(4)	C23−C24	1.385(4)
C19−C24	1.420(4)	C25−C26	1.415(4)	C26−C27	1.401(4)	C27−C28	1.385(4)
C28−C29	1.412(4)	C29−C30	1.386(4)	C30−C25	1.417(4)	C31−C32	1.504(4)
C32−C33	1.444(4)	C33−C34	1.352(4)	C34−C35	1.463(4)	C35−C36	1.346(4)
C31−C36	1.467(4)						
Bond angles [°]							
O1−Sr−O2	124.6(1)	O2−Sr−O4	93.7(1)	O1−Sr−O4	139.0(1)	O2−Sr−O3	90.3(1)
O1−Sr−O3	81.0(1)	O4−Sr−O3	115.8(1)	O2−Sr−O6	80.4(1)	O1−Sr−O6	87.7(1)
O3−Sr−O6	157.7(1)	O2−Sr−O5	140.2(1)	O6−Sr−O5	115.4(1)	O1−Sr−O5	93.6(1)
O4−Sr−O5	54.6(1)	O3−Sr−O5	84.6(1)	O6−Sr−O4	85.2(1)	O2−Sr−N1	62.2(1)
O1−Sr−N1	62.5(1)	O2−Sr−N2	79.8(1)	O1−Sr−N2	134.5(1)	O2−Sr−N3	133.8(1)
O1−Sr−N3	77.8(1)	O4−Sr−N1	150.8(1)	O3−Sr−N1	82.7(1)	O4−Sr−N2	58.7(1)
O3−Sr−N2	59.2(1)	O4−Sr−N3	64.1(1)	O3−Sr−N3	135.4(1)	O6−Sr−N1	75.1(1)
O5−Sr−N1	154.3(1)	O6−Sr−N2	137.1(1)	O5−Sr−N2	63.7(1)	O6−Sr−N3	58.9(1)
O5−Sr−N3	58.5(1)	N1−Sr−N2	125.9(1)	N2−Sr−N3	114.5(1)	N1−Sr−N3	119.6(1)

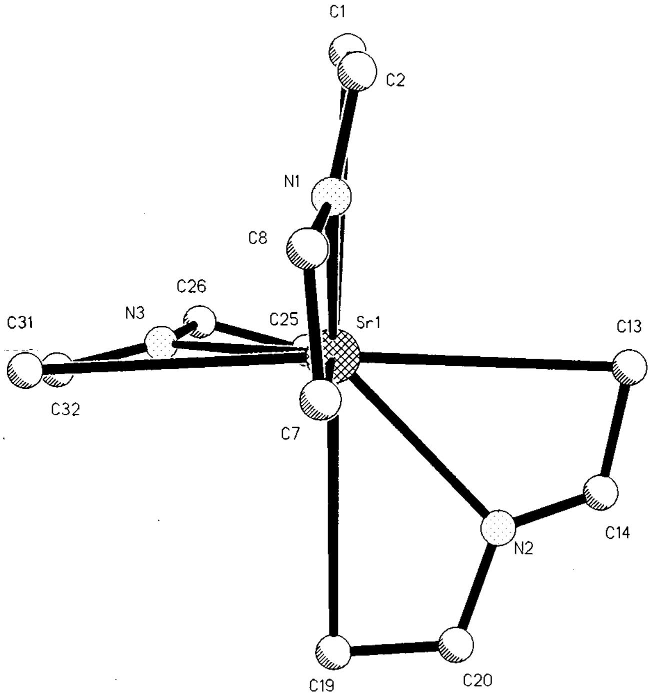


Figure 4. The core structure of the strontium complex **6** showing a helix of three paddles, the four carbon and nitrogen atoms being coplanar

diffraction studies of the gallium and aluminium compounds were performed with an Enraf-Nonius CAD4 diffractometer [λ(Mo-K_α) = 0.71073 Å, monochromator: graphite, $T = 293(2)$ K, $\omega-2\theta$ scan]. Cell parameters were determined by least-squares refinement of diffractometer angles for 24 automatically centred reflections. The X-ray diffraction study of the strontium compound **6** was performed with a Siemens P4 instrument equipped with a CCD area detector and a low-temperature device LTP2. The unit cell was determined from the data for 75 frames and data collection was performed in the hemisphere mode with $\Delta\varphi = 0-3°$, 10 s/frame exposures. Data reduction used the program SAINT. The structures were solved by direct methods (SHELXL-86). The experimental parameters are listed in Table 6. Atom H of compound **6** was found in the difference Fourier and refined freely including U_i. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-114655 to -114657. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: int. code + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

[Bis(3,5-di-*tert*-butyl-2-hydroxy-2-phenyl)amine]boron Chloride (1): A solution of 0.50 g (0.54 mmol) of Zn[3,5-di-*tert*-butyl-1,2-quinone (3,5-di-*tert*-butyl-2-hydroxy-1-phenyl)imine]$_2$[11] in 20 mL of dry benzene was treated dropwise at room temperature and under vigorous stirring with BCl3·DMS (96 mg, 0.54 mmol). Additional stirring for 5 h afforded a suspension. The $ZnCl_2$ formed was filtered and the solvents were removed at reduced pressure to leave a violet powder. The powder was washed with hexane to obtain 0.156 g of **1** (63%). − ^{11}B NMR: $\delta = +14.9$. − IR (KBr): $\tilde{\nu} = 2960$ cm^{-1}, 1458, 1420, 1364, 1202, 1036, 876, 670 and 474. − MS; *m*/*z*: 469 [M$^+$] (calcd. 469). − $C_{28}H_{41}BClNO_2$ (469.81): calcd. C 71.05, H 2.98, N 8.79; found C 71.05, H 2.51, N 8.35.

Aluminium Complex 2: A solution of 1.33 g (6.0 mmol) of 3,5-di-*tert*-butylcatechol in 30 mL of 95% ethanol was added to a solution of 0.36 g (1.5 mmol) of aluminium chloride hexahydrate in 15 mL of 95% ethanol. After the addition of 2 mL of 25% aqueous ammonia and stirring for 5 h, the solution became dark green. After 3 d, the crystalline product was filtered and washed with 5 mL of water and 3 mL of ethanol and dried under vacuum. Recrystallization from $CHCl_3$ yielded pure **2**, m.p. 240°C (1.17 g, 90%). − IR

Table 6. Crystallographic data for the complexes **2**, **3**, and **6**; disorder of the *tert*-butyl groups was found for the aluminium and gallium compounds

Compound	**2**	**3**	**6**
Empirical formula	$C_{56}H_{80}AlN_2O_4$	$C_{56}H_{80}GaN_2O_4$	$C_{84}H_{120}N_30_6Sr$
Molecular mass	872.20	914.94	1355.45
Space group	*P*−1	*P*−1	*P*2(1)/*c*
Crystal size [mm^3]	0.3 × 0.2 × 0.2	0.3 × 0.2 × 0.1	0.2 × 0.2 × 0.2
a [Å]	11.446(2)	11.592(2)	13.4814(1)
b [Å]	12.314(2)	12.323(2)	28.1594(4)
c [Å]	20.777(4)	20.737(2)	22.7799(1)
α [°]	90.08(3)	89.43(3)	90
β [°]	105.03(3)	105.73(3)	104.9270(1)
γ [°]	104.18(3)	104.27(3)	90
V [Å]	2735.5(8)	2758.1(8)	8356.07
Z	2	2	4
Linear abs. coeff. [mm^{-1}]	0.080	0.541	0.694
D_c [g ml^{-3}]	1.059	1.102	1.077
2θ limits [°]	5.14 to 36.24	4.40−50.26	2.90−58.88
Octants collected	−10, 9; −10, 10; 0, 18	−13, 13; −14, 0; −24, 24	−15, 17;−35, 35;−29, 29
No. of data collected	3976	10251	48989
No. of unique data collected	3820(R_{int} = 0.0164)	9756 (R_{int} = 0.0354)	15425(R_{int} = 0.0488)
No. of unique data used	2838 [$F > 4\sigma(F)$]	5478 [$F > 4\sigma(F)$]	10708 [$F > 4\sigma(F)$]
Intensity variation (σ)	> 4	> 4	> 4
R	0.0620	0.0582	0.0530
Rw	0.1512	0.1538	0.0916
Goodness of fit	1.120	1.036	1.113
No. of variables	568	568	847
$\Delta\rho_{min}$ [e A^{-1}]	−0.364	−0.555	−0.338
$\Delta\rho_{max}$ [e A^{-1}]	0.454	0.908	0.525

(KBr): ṽ = 2956 cm^{-1}, 2868, 1576, 1560, 1526, 1490, 1424, 1392, 1362, 1244, 1162, 1092, 970, 904, 858 and 736. − $C_{56}H_{80}AlN_2O_4$ (872.06): calcd. C 77.11, H 9.25, N 3.21; found C 77.16, H 9.22, N 3.21.

Gallium, Calcium, Barium, and Strontium Complexes 3−6: A similar procedure as for compound **2** was applied. − **3**: dark crystals obtained from CH_2Cl_2/ethanol. m.p. > 300°C (85% yield). − $C_{56}H_{80}GaN_2O_4$ (914.81): calcd.C 73.44, H 8.81, N 3.06; found C 73.16, H 8.98, N 3.08. − **4**: dark powder, m.p. 230°C (78% yield). − IR (KBr): ṽ = 2958 cm^{-1}, 2870, 1550, 1526, 1478, 1458, 1394, 1360, 1294, 1174, 1096, 994, 932, 860 and 732. − $C_{56}H_{80}CaN_2O_4$ (885.16): calcd. C 75.97, H 9.11, N 3.16; found C 76.01, H 9.13, N 3.22. − **5**: dark blue powder, m.p. 138°C (70% yield). − IR (KBr): ṽ = 2960 cm^{-1}, 2868, 1544, 1520, 1478, 1456, 1398, 1360, 1274, 1180, 1098, 994, 932, 864 and 732. − $C_{56}H_{80}BaN_2O_4 \cdot H_2O$ (1000.38): calcd. C 67.26, H 8.26, N 2.80; found C 67.27, H 8.21, N 2.85. − **6**: dark blue crystals m.p. 186°C (75% yield). − IR (KBr): ṽ = 2958 cm^{-1}, 2858, 1542, 1522, 1478, 1458, 1394, 1360, 1282, 1180, 1096, 994, 932, 896 and 732. − $C_{84}H_{120}SrN_3O_6 \cdot CH_2Cl_2$ (1440.16): calcd. C 70.88, H 8.53, N 2.92; found C 70.75, H 8.71, N 2.92.

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