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Synthesis and Molecular Structure of a Mononuclear Barium Aryloxide–Ethanolamine Complex, $Ba(2,6\text{-}Bu^t_2C_6H_3O)_2(HOCH_2CH_2NMe_2)_4\cdot 2C_7H_8$, Exhibiting Extensive Hydrogen Bonding

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The reaction of barium metal granules in tetrahydrofuran with 2,6-di-*tert*-butylphenol, utilizing gaseous ammonia as a catalyst, followed by addition of hexamethylphosphoramide, yields a monomeric barium species. The corresponding reaction of barium metal granules, 2-(dimethylamino)ethanol, and 2,6-di-*tert*-butylphenol in toluene yields an identical compound. The species has been characterized by IR, ^1H NMR, and ^{13}C NMR spectroscopy and single-crystal X-ray studies and shown to be the monomeric barium complex $Ba(2,6\text{-}Bu^t_2C_6H_3O)_2(HOCH_2CH_2NMe_2)_4\cdot 2C_7H_8$. Eight-coordination of the metal center is achieved through the agency of the four alcohol and four amino groups of the ethanolamine ligands. The bulky aryloxide anions are hydrogen-bonded to the OH groups of ethanolamine ligands. Crystal data at −154 °C: $a = 17.168$ (2) Å, $b = 33.364$ (5) Å, $c = 21.606$ (3) Å, $d_{calcd} = 1.169$ g cm^3, $Z = 8$, space group *Fd2d*.

Introduction

The interest in the formation and chemistry of main-group alkoxides and aryloxides has undergone a renaissance over the last 5 years.[1] There are many reasons for the renewed interest in this area. With the discovery of superconducting high-T_c ceramic materials in 1986, the inorganic chemist is now becoming more materials oriented.[2] An alternative to the traditional ceramicist's route for the preparation of metal oxide based materials is the use of metal alkoxides. As molecular precursors, these species offer certain advantages: they are soluble in organic solvents, it is possible to obtain some degree of stoichiometric control of the desired molecular aggregate, there are no ionic impurities present in the product, and, most importantly, these materials may yield low-temperature routes to metal oxides via thermolysis, sol–gel hydrolysis, or MOCVD processes.[3]

Alkoxides or aryloxides of the heavier alkaline-earth metals (Ca, Sr, or Ba) have received little attention to date,[4,5] which is rather surprising, given the large amount of research on the corresponding copper and lanthanide alkoxides.[1,6,7] Barium is an important constituent in oxides of wide-ranging properties and utility, e.g. $BaTiO_3$, $YBa_2Cu_3O_{7-x}$, and $Ba_{0.6}K_{0.4}BiO_3$, but virtually nothing is known concerning its aryloxides.

In the interest of making a volatile mononuclear barium aryloxide, we chose to use the sterically hindered ligand 2,6-di-*tert*-butylphenol. This bulky phenol has found widespread use in both main-group chemistry and transition-metal chemistry, stabilizing elements in low coordination numbers.[8-10]

We describe here the preparation of $Ba(OC_6H_3\text{-}2,6\text{-}Bu^t_2)_2(HOCH_2CH_2NMe_2)_4$ by the reaction of barium metal, suspended in THF, with 2,6-di-*tert*-butylphenol, utilizing gaseous ammonia as a catalyst, followed by the addition of HMPA. Alternatively, the reaction of barium metal with 2,6-di-*tert*-butylphenol and 2-(dimethylamino)ethanol yields the same product.

Results

Synthesis. The reaction of barium metal granules with 2,6-di-*tert*-butylphenol in THF *cannot* be initiated by heating, even for extended periods of time. Likewise, the use of a high-energy ultrasonic gun (with either stepped or tapered tips) fails to activate the metal. The addition of trace amounts of $HgCl_2$ or I_2 (known to activate metal surfaces) similarly failed to stimulate any reaction.

The alkaline-earth metals, like their counterparts the alkali metals, are known to dissolve in liquid NH_3 to yield amide complexes,[11] which, though poorly characterized, have provided active systems for reactions with a wide range of organic ligands that contain acidic protons.[12,13] The limitations behind such synthetic strategies is that products are obtained in only moderate (<65%) yield, due to the formation of insoluble $Ba(NH_2)_2(NH_3)_n$ as a byproduct. Recently, NH_3-saturated (rather than liquid NH_3) solutions have found some synthetic utility.[14] Indeed, it is known that NH_3 gas dissolves in ethereal solvents (i.e. diethyl ether or tetrahydrofuran), toluene, and benzene at room temperature to yield saturated solutions, containing >25% ammonia.[15,16] Surprisingly, this observation has found little synthetic utility until now.

We considered that the absence of a reaction between 2,6-di-*tert*-butylphenol and barium metal resulted from a negligible rate of reaction of the sterically encumbered aryloxide at the barium metal surface. We postulated that the smaller and more polar ammonia would react more rapidly in solution to yield a metal amide and hydrogen gas. If this reaction is performed in the presence of the phenol, then a facile ligand exchange should occur to yield the aryloxide. Thus ammonia gas catalyzes the heterogeneous reaction.

In reality, a more complex reaction occurred. The reaction of barium metal granules with 2,6-di-*tert*-butylphenol and THF, using NH_3 gas as a catalyst, yielded a white insoluble solid. This material was then dissolved by the addition of hexamethylphosphoramide (HMPA, $(NMe_2)_3P{=}O$), to yield $Ba(OC_6H_3$-

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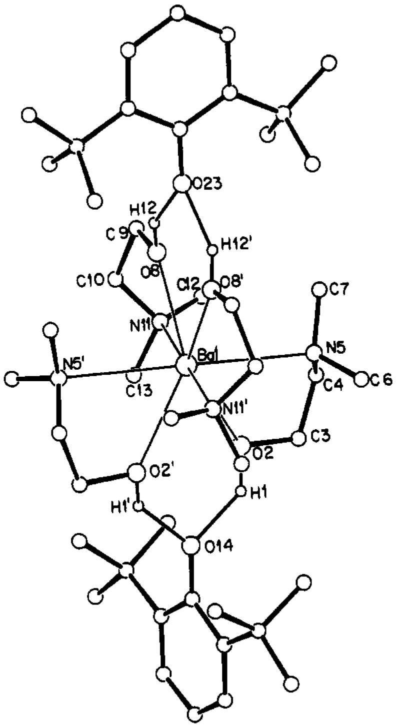

Figure 1. ORTEP drawing of $Ba(OC_6H_3\text{-}2,6\text{-}Bu^t_2)_2(HOCH_2CH_2NMe_2)_4$, showing selected atom labeling. The crystallographic C_2 axis passes through O(14), Ba(1), and O(23). Unlabeled atoms follow the sequence shown.

$2,6\text{-}Bu^t_2)_2(HOCH_2CH_2NMe_2)_4$ (I). The compound was readily crystallized from hot toluene over a period of 12 h to yield large regular-shaped crystals. The crystalline complex $Ba(OC_6H_3\text{-}2,6\text{-}Bu^t_2)_2(HOCH_2CH_2NMe_2)_4$ (I) was obtained as a toluene solvate and is readily soluble in benzene, toluene, THF, and CH_2Cl_2. It may also be prepared via the direct route involving barium metal, 2,6-di-*tert*-butylphenol, and 2-(dimethylamino)ethanol in excellent yield at room temperature. This complex is moderately air and moisture sensitive, turning dark green upon exposure to the atmosphere. Similar observations have been reported by Lappert and co-workers for $AlMe(OC_6H_3\text{-}2,6\text{-}Bu^t_2)_2$.[10]

The ^1H NMR spectrum of I in benzene-d_6 at 25 °C shows a singlet for the Bu^t groups, a singlet for the dimethylamino group, and two triplets for the methylene groups. The hydroxyl proton is observed at δ 4.69. Integration establishes the number of ethanolamine molecules as 4 vs the *tert*-butyl singlet. The ^{13}C NMR spectrum of I in benzene-d_6 at 25 °C reveals a single *tert*-butyl environment and likewise a single ethanolamine environment (one methyl and two methylene chemical shifts). The NMR spectra remain unchanged on cooling down to −80 °C in toluene-d_8. Hence, it is not possible to obtain limiting spectra in the temperature range +25 to −80 °C in toluene-d_8.

The melting point of I was found to be 94–97 °C. The reversibility of this process was determined by differential scanning calorimetry, which demonstrates this to be a true melting point.

The unexpected appearance of the ethanolamine ligand in I is established by ^1H and ^{13}C NMR studies in benzene-d_6. Free $Me_2NCH_2CH_2OH$ was liberated upon hydrolysis of I and was further characterized by comparison with an authentic sample by ^1H and ^{13}C NMR spectroscopy. This ligand was *not* present as an impurity in either the THF or HMPA employed in the synthesis of I. Evidently, this ligand is synthesized during the reaction. We have shown previously that barium can cleave THF to yield diols, e.g. $HOC(Et)_2CH_2OH$.[17] It seems probable that a first step is cleavage of THF (eq 1), such a reaction having precedent.[18] The organobarium product of eq 1 (or a hydrido enolate product of this formula) may then react with HMPA to couple carbon to an NMe_2 group.

$$Ba + C_4H_8O \xrightarrow{NH_3} (BaCH_2CH_2O)_n + CH_2{=}CH_2 \quad (1)$$

Table I. Fractional Coordinates[a] and Isotropic Thermal Parameters for $Ba(OAr)_2(HOCH_2CH_2NMe_2)_4{\cdot}2C_7H_8$

atom	x	y	z	$10B_{iso}$, Å^2
Ba(1)	10000*	5054*	5000*	14
O(2)	10633 (4)	5743 (2)	5465 (3)	24
C(3)	11349 (4)	5758 (2)	5803 (3)	25
C(4)	11569 (5)	5342 (2)	6008 (4)	27
N(5)	11654 (4)	5058 (2)	5483 (3)	33
C(6)	12356 (6)	5160 (4)	5133 (6)	64
C(7)	11697 (7)	4653 (3)	5733 (7)	64
O(8)	9531 (4)	4368 (2)	5553 (3)	24
C(9)	9148 (4)	4337 (2)	6132 (3)	24
C(10)	8813 (5)	4742 (2)	6286 (4)	25
N(11)	9405 (5)	5055 (2)	6316 (3)	41
C(12)	9874 (9)	4998 (6)	6881 (5)	81
C(13)	9029 (11)	5450 (3)	6323 (8)	88
O(14)	10000*	6376 (4)	5000*	18
C(15)	10000*	6759 (5)	5000*	22
C(16)	9492 (4)	6992 (2)	5404 (4)	13
C(17)	9509 (5)	7410 (3)	5390 (4)	20
C(18)	10000*	7618 (6)	5000*	22
C(19)	8942 (5)	6771 (2)	5853 (4)	21
C(20)	8441 (5)	7064 (2)	6240 (4)	27
C(21)	9439 (5)	6527 (2)	6335 (3)	27
C(22)	8378 (4)	6491 (2)	5508 (4)	27
O(23)	10000*	3732 (4)	5000*	17
C(24)	10000*	3322 (4)	5000*	21
C(25)	10633 (6)	3119 (3)	5280 (4)	21
C(26)	10615 (6)	2696 (3)	5264 (4)	22
C(27)	10000*	2488 (7)	5000*	26
C(28)	11302 (5)	3336 (2)	5601 (4)	23
C(29)	11875 (5)	3038 (2)	5919 (4)	29
C(30)	10980 (5)	3611 (2)	6124 (3)	27
C(31)	11770 (4)	3585 (2)	5134 (3)	24
C(32)	13820 (8)	5972 (5)	4607 (7)	59 (3)
C(33)	13573 (8)	5800 (4)	4061 (6)	65 (3)
C(34)	13464 (8)	6024 (4)	3514 (6)	50 (3)
C(35)	13653 (6)	6446 (3)	3536 (4)	41 (2)
C(36)	13885 (7)	6601 (4)	4084 (6)	49 (3)
C(37)	13981 (8)	6379 (4)	4613 (6)	66 (3)
C(38)	13551 (8)	6702 (4)	2971 (6)	53 (3)
H(1)	1086 (15)	621 (8)	511 (11)	226 (58)
H(12)	955 (4)	414 (2)	537 (3)	13 (12)

[a] Fractional coordinates are $\times 10^4$ for non-hydrogen atoms and $\times 10^3$ for hydrogen atoms. Parameters marked by an asterisk (*) were not varied.

Also significant is the observation that the reaction between barium, 2,6-di-*tert*-butylphenol, and $Me_2NCH_2CH_2OH$ yields an identical product. The use of a difunctional alcohol, one with a Lewis base incorporated into the hydrocarbon chain, dramatically increases the rate of reaction with barium metal. Although similar difunctional alcohols have been widely used in yttrium,[6] bismuth,[7] and copper alkoxide chemistry,[19] no explanations for this dramatic increase in rate of metal dissolution have yet been proposed.

Solid-State and Molecular Structure. Atomic positional parameters are given in Table I. The complex $Ba(OC_6H_3\text{-}2,6\text{-}Bu^t_2)_2(HOCH_2CH_2NMe_2)_4$ (I) crystallizes from toluene solutions with two molecules of toluene solvent (C(32)–C(38) in Table I). A ball-and-stick drawing of I giving the atom-numbering scheme is given in Figure 1, and pertinent bond distances and bond angles are given in Table II.

The structure of I consists of monomeric units in which the primary coordination about the barium atom is a distorted dodecahedral geometry. The two orthogonal trapezoidal units of an ideal dodecahedron would each be planar. In $Ba(OC_6H_3\text{-}2,6\text{-}Bu^t_2)_2(HOCH_2CH_2NMe_2)_4$ they are significantly nonplanar

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Table II. Selected Bond Distances (Å) and Angles (deg) for $Ba(OC_6H_3\text{-}2,6\text{-}Bu^t_2)_2(HOCH_2CH_2NMe_2)_4\cdot 2C_7H_8$

Distances			
Ba(1)–O(2)	2.733 (7)	O(2)–H(1)	1.79 (26)
Ba(1)–O(8)	2.704 (6)	H(1)–O(14)	1.59 (25)
Ba(1)–N(5)	3.026 (6)	O(8)–O(23)	2.57 (14)
Ba(1)–N(11)	3.022 (6)	O(8)–H(12)	0.85 (8)
O–C(av)	1.373 (3)	H(12)–O(23)	1.76 (8)
O(2)–O(14)	2.58 (13)		
Angles			
O(2)–Ba(1)–O(2)′	65.60 (27)	N(11)–Ba(1)–N(11)′	179.91 (26)
O(2)′–Ba(1)–O(8)	139.04 (17)	Ba(1)–O(2)–C(3)	124.1 (5)
O(2)–Ba(1)–O(8)	131.85 (16)	Ba(1)–O(8)–C(9)	126.3 (5)
O(2)–Ba(1)–N(5)′	119.77 (19)	Ba(1)–N(5)–C(4)	100.0 (4)
O(2)–Ba(1)–N(5)	59.75 (18)	Ba(1)–N(5)–C(6)	126.6 (7)
O(2)–Ba(1)–N(11)′	102.18 (22)	Ba(1)–N(5)–C(7)	99.8 (5)
O(2)–Ba(1)–N(11)	77.75 (19)	Ba(1)–N(11)–C(10)	101.1 (4)
O(8)–Ba(1)–O(8)′	64.43 (26)	Ba(1)–N(11)–C(12)	126.4 (6)
O(8)–Ba(1)–N(5)′	82.89 (19)	Ba(1)–N(11)–C(13)	99.1 (6)
O(8)–Ba(1)–N(5)	97.54 (21)	C(3)–O(2)–H(1)	90.0 (8)
O(8)′–Ba(1)–N(11)	121.15 (20)	Ba(1)–O(8)–H(12)	123.0 (5)
O(8)–Ba(1)–N(11)	58.93 (19)	C(9)–O(8)–H(12)	111.0 (5)
N(5)–Ba(1)–N(5)′	179.50 (26)	O(2)–H(1)–O(14)	99.5 (0)
N(5)′–Ba(1)–N(11)	90.41 (22)	O(8)–H(12)–O(23)	156.3 (2)
N(5)–Ba(1)–N(11)	89.59 (22)		

Table III. Crystal Data for $Ba(OC_6H_3\text{-}2,6\text{-}Bu^t_2)_2(HOCH_2CH_2NMe_2)_4\cdot 2C_7H_8$

formula	$C_{44}H_{86}BaN_4O_6\cdot 2C_7H_8$	space group	*Fd2d*
a, Å	17.168 (2)	*T*, °C	−154
b, Å	33.364 (5)	λ, Å	0.71069
c, Å	21.606 (3)	d_{calcd}, g cm^3	1.169
V, Å^3	12376.17	μ(Mo Kα), cm^{-1}	6.85
Z	8	*R*(F)	0.046
fw	1088.81	$R_w(F)$	0.047

(O(2), O(2)′, N(5), and N(5)′ deviate by as much as ±0.47 Å, and O(8), O(8)′, N(11), and N(11)′ deviate by ±0.29 Å), but each has Ba in the respective least-squares plane and these two planes meet at an angle of 92.0°. Noteworthy is the fact that Ba and the four nitrogens are coplanar to within 0.01 Å.

The aryloxide groups do not bind directly to barium. The Ba^{2+} displays interactions with the four oxygen and four nitrogen atoms of the four bidentate $NMe_2CH_2CH_2OH$ ligands. The Ba–N distances are found in the range 3.022–3.026 Å, and the Ba–O distances are slightly shorter, 2.704–2.733 Å. A crystallographic 2-fold axis relates the two independent ethanolamine ligands, but the idealized symmetry is S_4. This leaves the Ba(chelating ligand)$_4$ with a +2 charge. The charge is compensated by hydrogen bonding from the nonbonded phenoxide oxygen atoms of 2,6-di-*tert*-butylphenoxide ligands.

Hydrogen bonding in this complex gives close O(2)–O(14) contacts of 2.58 (13) Å and O(8)–O(23) at 2.57 (14) Å, for the two phenoxide moieties. The longer distances O(23)–H(12) of 1.76 Å and O(2)–H(1) of 1.79 Å mark these as phenoxide oxygens. (Compare the O(8)–H(12) distance of 0.85 Å and the O(14)–H(1) distance of 1.59 Å; hence, these are the alcohol ligands, e.g. $Me_2NCH_2CH_2OH$).

This molecule may be compared to other known alkaline-earth phenoxides that exhibit hydrogen bonding. The complex $Ca(OC_6H_3\text{-}2,4\text{-}(NO_2)_2)_2\cdot 7H_2O$ consists of a central calcium bonded to eight oxygen atoms, two from the phenoxide atoms (the phenoxy oxygen and one nitro oxygen) and six from water molecules, one of which bridges two adjacent calcium atoms.[20] The remaining phenoxide is hydrogen-bonded to the coordinated water molecules, with a multitude of hydrogen-bonding opportunities between this nonbonded phenoxide and water oxygen atoms.

In contrast to the case of calcium above, the corresponding magnesium complex is octahedrally coordinated to six water molecules.[20] The 2,4-dinitrophenoxide anions are not directly bound to magnesium but are hydrogen-bonded to the coordinated water molecules. These molecules differ from I also in their synthesis, in that they were prepared in aqueous media.

Concluding Remarks

An attempt to prepare a barium phenoxide of small aggregation employing the sterically demanding 2,6-di-*tert*-butylphenoxide failed in a most interesting and unexpected manner. The facile degradation of HMPA and THF in the presence of barium is quite remarkable and to our knowledge is without precedent as a preparation of 2-(dimethylamino)ethanol. The molecular structure of the resultant complex $Ba(OC_6H_3\text{-}2,6\text{-}Bu^t_2)_2(Me_2NCH_2CH_2OH)_4$ reveals a central BaO_4N_4 moiety with strong hydrogen bonding from the hydroxyl hydrogen atom to the phenoxide oxygen atoms. The Ba to O distances involving the phenoxide oxygen atoms are 4.41 Å, and this charge separation is presumably compensated by the combined effects of chelating and hydrogen bonding. The use of ammonia gas as a catalyst may be extended to other metals known to dissolve in liquid ammonia, e.g. aluminum, thallium, and certain lanthanides.[21]

Experimental Section

All manipulations were carried out under an atmosphere of dry (molecular sieves) argon, with rigorous exclusion of air and moisture. All hydrocarbon and ethereal solvents were dried and distilled from sodium benzophenone ketyl. NMR solvents were dried over 4-Å molecular sieves and stored under argon. Barium metal, 2,6-di-*tert*-butylphenol, and *N,N*-dimethylethanolamine (freshly distilled and dried over 4-Å molecular sieves) were purchased from the Aldrich Chemical Co. and stored in a drybox under an argon atmosphere. Elemental analyses were performed by Oneida Research Services. NMR data were recorded on a Bruker WM-500 NMR spectrometer, using the protio impurities of the deuterated solvents as reference for ^1H and the ^{13}C chemical shifts. Infrared spectra were recorded on a Nicolet 510P FTIR spectrometer, as Nujol mulls between KBr plates.

Synthesis of $Ba(OAr)_2(HOCH_2CH_2NMe_2)_4\cdot 2C_7H_8$ (I). Barium metal granules (1.37 g, 10 mmol) $2,6\text{-}Bu^t_2C_6H_3OH$ (4.12 g, 20 mmol) and THF (20 mL) were stirred together for 10 min in a Schlenk tube until all the ligand has dissolved. Ammonia gas was bubbled into the reaction mixture for 10 min, during which time the *rapid* evolution of gas bubbles was observed, indicating that the barium metal was reacting. The solution was then stirred for 3 h, during which time all the metal was consumed to yield a white suspension. Hexamethylphosphoramide (3.5 mL, 20 mmol) was added to dissolve the precipitate, yielding a cloudy brown solution. The solvent and excess ammonia were removed under vacuum to yield a white solid. This was redissolved in hot toluene (15 mL), and the mixture was filtered. The filtrate was left to crystallize at room temperature (20 °C) for 12 h, during which time a large crop of colorless crystals formed. Yield = 6.58 g, 78% based on Ba.

Alternate Synthesis of I. Barium metal granules (1.37 g, 10 mmol) and $2,6\text{-}Bu^t_2C_6H_3OH$ (4.12 g, 20 mmol) were stirred in toluene for 10 min in a Schlenk tube until all the ligand dissolved. The Schlenk tube was then cooled to 0 °C and $Me_2NCH_2CH_2OH$ (5.07 mL, 40 mmol) added via syringe. An exothermic reaction resulted in vigorous gas evolution, with all the metal being consumed in 1 h. The solvent was removed under vacuum to yield a waxy white solid. This was subsequently redissolved in hot toluene (15 mL), and the mixture was filtered. The filtrate was left to crystallize at 5 °C for 14 h, during which time a large crop of colorless crystals formed. Yield = 5.86 g, 71% based on Ba.

Spectroscopic and Analytical Data. IR (Nujol, cm^{-1}): 3100 br. Mp 94–97 °C, decomposition at >110 °C. ^1H NMR (500 MHz, 25 °C, benzene-d_6): δ 1.43 (s, Bu^t), 1.95 (s, NMe_2), 2.16 (t, CH_2), 3.56 (t, CH_2), 4.69 (s, OH), 6.83 (t, Ph), 6.97 (m, Ph), 7.09 (m, Ph), 7.23 (m, Ph). ^{13}C NMR (126 MHz, 25 °C, benzene-d_6): δ 30.62 (s, Bu^t), 34.62 (s, $\mathit{C}Me_3$), 45.04 (s, NMe_2), 59.02 (s, CH_2), 62.14 (s, CH_2), 125.23 (s, Ph), 126.06 (s, Ph), 128.93 (s, Ph), 129.69 (s, Ph), 136.38 (s, Ph). Anal. Calcd for $BaO_6N_4C_{58}H_{102}$: C, 63.93; H, 9.37; N, 5.14. Found: C, 63.71; H, 9.49; N, 5.32.

Crystallographic Studies. General operating procedures and listing of programs have been previously described.[22] A summary of crystallographic data is given in Table III.

$Ba(OC_6H_3Bu^t_2)_2(HOCH_2CH_2NMe_2)_4\cdot 2C_7H_8$. A suitable crystal was selected and transferred to the goniostat, where it was cooled to −154 °C for characterization and data collection (Table III). A systematic search

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of a limited hemisphere of reciprocal space yielded a set of reflections that exhibited orthorhombic symmetry. The general reflection conditions of $h + k$, $h + l$, and $k + l = 2n$ for hkl indicated an F-centered lattice. The further general conditions for $0kl$ of $k + l = 4n$ with h and k both even, for $hk0$ of $h + k = 4n$ with h and k both even, and for $h0l$ of $h + l = 4n$ with k and l both even lead to the choice of the space group *Fd2d*, an alternate setting of space group No. 43, *Fdd2*. Unit cell dimensions were determined by using 62 unique reflections having 2θ between 15 and 35°. Subsequent solution and refinement of the structure confirmed the choice of *Fd2d*. No absorption correction was carried out.

The structure was solved by locating the Ba atom from a Patterson function and was confirmed by direct methods. The remaining non-hydrogen atoms were located by using several difference Fourier maps. The Ba atom is located on a crystallographic 2-fold axis. It is coordinated to two independent (by symmetry four) bidentate ligands: $HOCH_2CH_2N(CH_3)_2$. Two 2,6-di-*tert*-butylphenolate groups are located on the 2-fold axis and are hydrogen-bonded to the O atoms in the HOR–ligands. The two aromatic rings are approximately perpendicular to each other (interplanar angle 74°). The asymmetric unit also contains one molecule of solvent toluene (C(32)–C(38)). Almost all of the hydrogen atoms were located in a difference Fourier map following the initial refinement of the structure. They were introduced in the final full-matrix least-squares refinement cycles in idealized fixed positions; only the two hydrogen atoms associated with the hydrogen bond were refined by using isotropic thermal parameters. No hydrogen atoms were introduced on the solvent molecule. All non-hydrogen atoms were refined by using anisotropic thermal parameters, except for those solvent atoms that were kept isotropic. The total number of variables was 286, giving a ratio of observations to variables of 12. The final difference map was essentially featureless. There were two peaks of about 1.6 e/Å^3 in the immediate vicinity of the Ba atom, and all other peaks were less than 0.5 e/Å^3. The closest approach of the solvent molecule to the Ba complex is 3.78 Å for C(33)–C(6).

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Supplementary Material Available: Tables of full crystallographic details, anisotropic thermal parameters, and complete bond distances and angles and drawings showing the complete atom-numbering scheme and vibrational ellipsoids (7 pages); a listing of F_o and F_c values (9 pages). Ordering information is given on any current masthead page.

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Tetradentate Dithiooxamide Ligands and Their Nickel Complexes. Synthesis, Characterization, and Crystal Structure of a Mononuclear Neutral Complex, $Ni((c\text{-}C_5H_9)NHC(S)C(S)N(CH_2)_2NC(S)C(S)NH(c\text{-}C_5H_9))$

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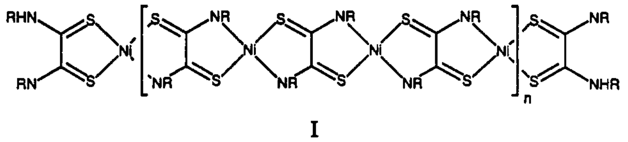
N-Monosubstituted dithiooxamides react in a 2:1 stoichiometry with diamines to give tetradentate dithiooxamide ligands (LH_4) of the general formula $RNHC(S)C(S)NH(CH_2)_nNHC(S)C(S)NHR$ ($R = c\text{-}C_5H_9$ and $c\text{-}C_6H_{11}$, $n = 2$; $R = n\text{-}C_{12}H_{25}$ and $C_6H_5CH_2$, $n = 2\text{–}4$). Reaction of these ligands with Ni(II) gives cationic complexes of the general formula $[Ni(LH_4)]^{2+}$ under acidic conditions, neutral complexes of formula $Ni(LH_2)$ under neutral conditions, and a polymeric material of approximate formula $(Ni_2L)_n$ under basic conditions. $Ni(LH_2)$ and $[Ni(LH_4)]Br_2$ can be interconverted by protonation/deprotonation under extreme conditions. Associated with this interconversion is a color change from red ($Ni(LH_2)$) to blue ($[Ni(LH_4)]Br_2$). Crystals of the neutral complex $Ni((c\text{-}C_5H_9)NHC(S)C(S)N(CH_2)_2NC(S)C(S)NH(c\text{-}C_5H_9))$ were grown from *n*-heptane/chloroform. This complex crystallizes in the orthorhombic space group *Pbcn* (No. 60) with cell dimensions $a = 25.152$ (9) Å, $b = 7.998$ (3) Å, $c = 9.865$ (5) Å, and $V = 1984.5$ (1) Å^3. For $Z = 4$ and a formula weight of 459.34, the calculated density is 1.537 g/cm^3. Diffraction data (Mo Kα) were collected with a Rigaku AFC5R diffractometer at 23 °C, and the structure was solved by the heavy-atom method. The final agreement factors were $R = 0.065$ and $R_w = 0.059$ for the 662 observed reflections.

Introduction

Dithiooxamide (DTO) and its mono- and disubstituted derivatives have a varied and interesting coordination chemistry, and their intense chromophores[1] have led to a number of applications,[2] including an important imaging process.[3] The DTO ligands are exemplary of polyfunctional molecules that can, in principle, chelate in a variety of different ways; i.e., they are *flexidentate* ligands.[4] Attention has focused especially on their intensely colored neutral polymeric, $[(ML')_n]$,[5] and cationic monomeric, $[M(L'H_2)_2]X_2$,[6] complexes ($L'H_2$ = substituted bidentate DTO ligand; X = halide, oxyanion) of the periodic group 10 elements: Ni, Pd, and Pt. The particular complex formed depends on the reaction conditions and stoichiometry.

In the case of nickel(II), 1 equiv of metal ion reacts with 1 equiv of $L'H_2$ in neutral or weakly acidic media to give a dark blue insoluble 1:1 polymer of undetermined molecular weight. In this material each ligand is believed to bridge between two nickel atoms, coordinating to each metal atom through one sulfur and one nitrogen, forming a five-membered chelate ring (see I).[5b,6b,7] It has been assumed that the chain terminates with the final DTO ligand coordinated in a bidentate S_2, rather than N,S, fashion.



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With 2 or more equivalents of $L'H_2$ and from strongly acidic media, salts of monomeric cationic nickel(II) complexes, of the

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