Table I. Activation and Thermodynamic Parameters for the Spin Relaxation of the Quintet/Singlet Equilibria of $Fe(pyim)_3^{2+}$ and $Fe(phenmethoxa)_2^{2+}$ in Acetone

param	units	$Fe(pyim)_3^{2+}$	$Fe(phenmethoxa)_2^{2+}$
K (25 °C)		0.56 ± 0.18	5.4 ± 2.0
τ	ns	45 ± 5	110 ± 10
$\Delta H°$	kcal/mol	3.8 ± 0.1[a]	5.7 ± 0.1
$\Delta S°$	cal/K·mol	11.6 ± 0.3[a]	22.5 ± 0.5
$\Delta\overline{V}$	cm³/mol	8.1 ± 1.3	12.3 ± 1.0
$\Delta V_{\tau^{-1}}^{\ddagger}$	cm³/mol	0.0 ± 0.5	2.0 ± 0.3
$\Delta H_{ls}^{\ddagger}$	kcal/mol	6.7 ± 0.3	7.8 ± 0.4
$\Delta H_{hs}^{\ddagger}$	kcal/mol	2.9 ± 0.3	2.1 ± 0.2
$\Delta V_{ls}^{\ddagger}$	cm³/mol	5.2 ± 2.0	3.9 ± 1.0
$\Delta V_{hs}^{\ddagger}$	cm³/mol	−2.9 ± 1.5	−8.4 ± 2.0

[a] Reference 10.

We have no ready explanation for the observation that $\Delta V_{hs}^{\ddagger}$ is much more negative for II than for I except to note that the coordination spheres are considerably different and to suggest that detailed interpretation of such differences should await measurement of $\Delta V_{hs}^{\ddagger}$ values for a broader range of compounds and conditions. Further investigations into the volume profiles of these and related systems are in progress.

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Articles

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Reactions of Coordinated β-Polyketonate Ligands. 1. Synthesis and Structure of Bis[1,7-diphenyl-1,3,4,5,7-heptanepentaonato(2−)]tetrakis(pyridine)dicobalt(II) Resulting from the Oxidation of Bis[1,7-diphenyl-1,3,5,7-heptanetetraonato(2−)]tetrakis(pyridine)dicobalt(II)

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The binuclear Co(II) complex of 1,7-diphenyl-1,3,5,7-heptanetetraone, H_3DBAA, was prepared and characterized as $Co_2(HDBAA)_2(py)_4$. The Co(II) ions reside at the 1,3 and 5,7 enolate positions with the potential third coordination site in the center vacant. Crystallization of this compound from 10% by volume pyridine in benzene in the air resulted in oxidation of the 4-carbon of both ligands to carbonyls. The structure of the crystalline oxidation product bis[1,7-diphenyl-1,3,4,5,7-heptanepentaonato-(2−)]tetrakis(pyridine)dicobalt(II)-4-pyridine, $Co_2(O{=}DBAA)_2(py)_4{\cdot}4py$ ($Co_2C_{78}H_{64}N_8O_{10}$), was determined by X-ray techniques. The crystal belongs to the triclinic space group $P1$ and has one molecule per unit cell. The lattice constants are a = 12.087 (7) Å, b = 12.435 (8) Å, c = 13.845 (9) Å, α = 67.71 (5)°, β = 70.76 (5)°, γ = 87.46 (5)°, and V = 1810 (2) Å³.

Introduction

The β-polyketones are a homologous series of molecules that are potentially valuable ligands in the study of polynuclear metal complexes. They combine the general coordinating ability of the simplest member, the 1,3-diketones, with the capability to form homologous transition-metal complexes. Thus, they afford the unusual opportunity to investigate the physical and chemical significance of systematically increasing the number of metal ions per molecule in a controlled chemical environment. Our laboratory has expended a considerable effort during the past several years investigating the synthesis, structure, magnetism, and electrochemical properties of the binuclear metal complexes of the 1,3,5-triketonates, the second member of the homologous series. However, the ligating properties of the third series member, the 1,3,5,7-tetraketonates, are essentially unknown. Two brief reports from our laboratory[1,2] constitute the only published reports of 1,3,5,7-tetraketonate complexes, the latter of which describes the structure of a heterotrinuclear complex containing two UO_2^{2+} ions and one Ni(II). In addition, a paper describing the synthesis, structure, and electrochemistry of a series of heterotrinuclear tetraketonates, $(UO_2)_2M^{II}(DBAA)_2(py)_4$ where M^{II} = Zn, Cu, Ni, Co, Fe, and Mn, is now available.[3] This report includes the single-crystal structure determination of the M^{II} = Ni, Co, Fe, and Mn complexes. To our knowledge, this is the only information currently available.

An underlying reason for investigating polynuclear transition-metal complexes is the possibility that the presence of two or more metal ions may impart unusual chemical properties to these molecules. The polynuclear Co(II) complexes are of considerable interest in this regard inasmuch as they may exhibit both Co(III) and Co(I) redox chemistry and certain related mononuclear species have well-developed O_2 chemistry.[4] Our initial studies of binuclear Co(II) complexes dealt with structural-magnetic relationships[5] followed by a report of the use of binuclear

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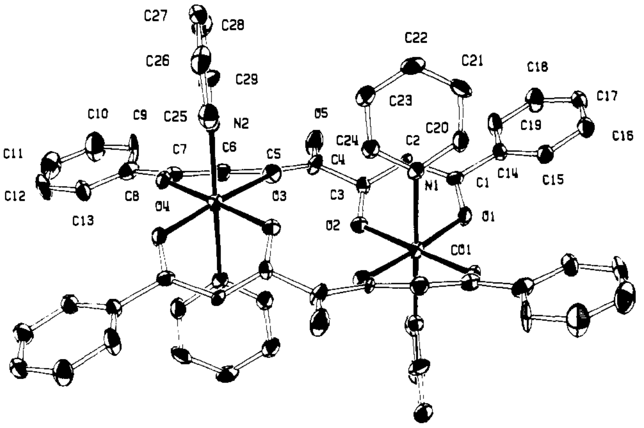

Figure 1. ORTEP drawing and atom-numbering scheme for $Co_2(O{=}DBAA)_2(py)_4$.

Co(II) complexes as catalysts in the oxidation of 3,5-di-*tert*-butylcatechol to the quinone.[6] For this reason, the facile ligand oxidation of the binuclear Co(II) 1,3,5,7-tetraketonate described below is of obvious interest to us.

The activation and reaction of methine carbons in macrocyclic cobalt complexes in which the ligand is formed by 2,4-pentanedione condensation with polyamines has been discussed recently by Endicott[7,8] and Goedken.[9] In these cases, the methine carbon is an atom in the six-membered chelate ring. Oxidation to a carbonyl destroys the enolate character of the ring; however, since the complexes are macrocyclic, they remain intact. In the current study, the oxidized complex also remains intact since the 4-carbon, which is oxidized, is not a member of an enolate chelate ring.

Experimental Section

Ligand Synthesis. The ligand 1,7-diphenyl-1,3,5,7-heptanetetraone, H_3DBAA, was prepared by methods developed by Harris and co-workers.[10]

Synthesis of $Co_2(HDBAA)_2(py)_4 \cdot H_2O$. A solution of 2.008 g (6.52×10^{-3} mol) of 1,7-diphenyl-1,3,5,7-heptanetetraone, H_3DBAA, and 2.7 mL (d = 0.726 g/mL) of $(C_2H_5)_3N$ in 100 mL of acetone was heated to reflux. An acetone solution of 2.332 g (9.80×10^{-3} mol) of $CoCl_2 \cdot 6H_2O$ was added dropwise to the refluxing ligand solution. Upon complete addition of the Co(II) solution, 3 mL of pyridine was added, after which a golden precipitate formed. This mixture was refluxed for 6 h, cooled to room temperature, and filtered, and the resulting solid was air-dried. Anal. Calcd for $C_{58}H_{50}N_4O_9Co_2$: C, 65.43; H, 4.70; N, 5.26; Co, 11.7. Found: C, 65.34; H, 4.78; N, 5.15; Co, 11.33.

Synthesis of $Co_2(O{=}DBAA)_2(py)_4$. The golden product, $Co_2(DBAA)_2(py)_4$, was dissolved in a solution of pyridine/benzene containing 10% by volume of pyridine. Slow evaporation of this solution in the air at room temperature resulted in oxidation of the ligand to 1,7-diphenyl-1,3,4,5,7-heptanepentaone yielding the binuclear complex bis[1,7-diphenyl-1,3,4,5,7-heptanepentaonato(2−)]tetrakis(pyridine)dicobalt(II)–4-pyridine, $Co_2(O{=}DBAA)_2(py)_4 \cdot 4py$. The dark red crystals isolated were suitable for X-ray analysis. The yield of this oxidized product is essentially quantitative.

Crystallography and Structure Determination. A suitable crystal of $Co_2(O{=}DBAA)_2(py)_4 \cdot 4py$ was mounted on a glass fiber with epoxy cement, covered with silicone grease to prevent loss of solvated pyridines, and placed on a Syntex P2$_1$ four-circle diffractometer. Rotation and axial photographs were used to determine the crystal system. Absorption (μ = 5.36 cm^{-1}) and extinction corrections were not made. A summary of the X-ray data collection parameters is given in Table I. The triclinic space group $P1$ was assumed and refinement carried out satisfactorily on that basis. No effort was made to find the nitrogen atoms of the lattice pyridines. They were refined as carbon atoms. The basic structure and atom-numbering scheme are presented in Figure 1. Atomic coordinates are listed in Table II. A listing of bond distances and angles has been deposited as supplementary material. Tables of the final positional and thermal parameters and the observed and calculated structure factors have also been deposited. Computer programs used may be found in ref 11.

Table I. X-ray Experimental Data for $Co_2(O{=}DBAA)_2(py)_4 \cdot 4py$

formula	$Co_2C_{78}H_{64}N_8O_{10}$
habit	rectangular prism
color	red
size, mm^3	$0.55 \times 0.50 \times 0.35$
cryst system	triclinic
space group	$P1$
ρ_{exptl}, g cm^{-3}	1.31
molecules/unit cell	1
radiation used	Mo Kα
wavelength, Å	0.710688
temp, °C	22
lattice constants	
a, Å	12.087 (7)
b, Å	12.435 (8)
c, Å	13.845 (9)
α, deg	67.71 (5)
β, deg	70.76 (5)
γ, deg	87.46 (5)
V, Å^3	1810 (2)
data collection	
monochromator	graphite
type of scan	$\theta/2\theta$
scan range, deg	Kα_1 − 1 to Kα_2 + 1
scan rate, deg/min	2
collection region	$\pm h,+k,+l$
2θ(max), deg	40
no. of reflcns measd[a]	3793
no. of std reflcns	3
how often measd	every 97 data
decay	~5%
data reduction	
corrections applied	Lp and decay
$\sigma(F_o^2)$[b]	$(\sigma_c^2 + 0.051F_o^2)^{1/2}$
obsd reflcn	$F_o^2 \geqslant 3\sigma(F_o^2)$
no. of unique obsd reflcns	1505
absorption	
μ, cm^{-1}	5.36
correction	none
solution method	F^2 Patterson
hydrogen atoms	
how located	calcd
bond dist, Å	0.95
arrangement	sp^2
iso thermal parameter	10% > C
refinement	
method	full-matrix least squares
wt	$w = [1/\sigma(F_o)]^2$
quantity minimized	$\Sigma w(\lvert F_o\rvert - \lvert F_c\rvert)^2$
non-H atoms	anisotropic
solvent atoms	isotropic
H atoms	fixed
no. of variables	382
R_1[d]	0.056
R_2[e]	0.059
S[f]	1.426
residual electron density, e/Å^3	0.5–0.6
scattering factors	ref 12–14

[a] This number includes standards and ψ-scan data. [b] σ is from counting statistics. [c] $R_m = \{\Sigma[\Sigma(F_o^2 - \langle F^2\rangle)^2]/\Sigma[\Sigma(F_o^2)^2]\}^{1/2}$. The angle brackets indicate an average of symmetry-equivalent intensities. The inner summations in both numerator and denominator are over symmetry equivalents, and the outer summations are over all symmetry-equivalent groupings. The R factor for averaging F^2 was 2.7%. [d] $R_1 = \Sigma[\lvert F_o\rvert - \lvert F_c\rvert]/\Sigma\lvert F_o\rvert$. [e] $R_2 = [\Sigma w(\lvert F_o\rvert - \lvert F_c\rvert)^2/\Sigma w\lvert F_o\rvert^2]^{1/2}$. [f] $S = [\Sigma w(\lvert F_o\rvert - \lvert F_c\rvert)^2/(NO - NV)]^{1/2}$, where NO is the number of observations and NV is the number of variable parameters.

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Table II. Atomic Coordinates[a] of the Non-Hydrogen Atoms of $Co_2(O{=}DBAA)_2(py)_4 \cdot 4py$

atom	*x*	*y*	*z*
Co(1)	−0.1161 (2)	0.1755 (2)	0.0409 (2)
O(1)	−0.2093 (7)	0.2906 (7)	−0.0471 (7)
O(2)	−0.0224 (7)	0.1579 (7)	−0.1051 (7)
O(3)	0.0240 (8)	−0.0558 (7)	−0.1205 (8)
O(4)	0.2117 (7)	−0.1849 (8)	−0.1899 (8)
O(5)	−0.0029 (9)	0.1566 (9)	−0.3567 (9)
N(1)	−0.2518 (11)	0.0358 (10)	−0.0787 (9)
N(2)	−0.0172 (9)	−0.3093 (10)	−0.0045 (13)
C(1)	−0.2276 (12)	0.2892 (11)	−0.1321 (11)
C(2)	−0.1620 (12)	0.2268 (11)	−0.1961 (11)
C(3)	−0.0653 (12)	0.1695 (11)	−0.1782 (12)
C(4)	−0.0003 (12)	0.1161 (13)	−0.2622 (13)
C(5)	0.0638 (12)	0.0065 (12)	−0.2203 (14)
C(6)	0.1615 (13)	−0.0088 (12)	−0.3038 (11)
C(7)	0.2281 (13)	−0.1078 (14)	−0.2843 (13)
C(8)	0.3233 (15)	−0.1242 (14)	−0.3779 (13)
C(9)	0.3216 (14)	−0.0721 (13)	−0.4849 (18)
C(10)	0.4117 (22)	−0.0849 (18)	−0.5716 (17)
C(11)	0.5005 (19)	−0.1514 (18)	−0.5542 (18)
C(12)	0.5003 (15)	−0.2058 (17)	−0.4466 (23)
C(13)	0.4125 (16)	−0.1926 (13)	−0.3581 (14)
C(14)	−0.3285 (13)	0.3558 (11)	−0.1580 (14)
C(15)	−0.4163 (15)	0.3744 (12)	−0.0768 (12)
C(16)	−0.5132 (13)	0.4299 (14)	−0.0982 (14)
C(17)	−0.5197 (13)	0.4684 (13)	−0.2018 (17)
C(18)	−0.4293 (17)	0.4535 (12)	−0.2862 (13)
C(19)	−0.3334 (13)	0.3967 (13)	−0.2646 (13)
C(20)	−0.3688 (16)	0.0496 (12)	0.1070 (11)
C(21)	−0.4525 (12)	−0.0318 (17)	0.1239 (13)
C(22)	−0.4157 (16)	−0.1328 (14)	0.1136 (13)
C(23)	−0.2976 (17)	−0.1503 (14)	0.0839 (13)
C(24)	−0.2199 (12)	−0.0637 (14)	0.0692 (11)
C(25)	−0.0628 (15)	−0.3949 (17)	0.0966 (15)
C(26)	−0.1436 (15)	−0.4878 (13)	0.1189 (16)
C(27)	−0.1735 (15)	−0.4855 (20)	0.0326 (24)
C(28)	−0.1291 (19)	−0.3976 (22)	−0.0687 (18)
C(29)	−0.0526 (15)	−0.3096 (13)	−0.0842 (13)
C(30)	0.1309 (15)	0.1015 (15)	0.3372 (14)
C(31)	0.2241 (15)	0.1046 (15)	0.2413 (14)
C(32)	0.3201 (15)	0.1867 (16)	0.1949 (14)
C(33)	0.3230 (14)	0.2669 (15)	0.2404 (14)
C(34)	0.2316 (17)	0.2690 (17)	0.3306 (16)
C(35)	0.1337 (16)	0.1857 (17)	0.3804 (15)
C(36)	−0.1102 (19)	0.4356 (20)	0.4297 (17)
C(37)	−0.2250 (19)	0.3865 (17)	0.4387 (16)
C(38)	−0.3118 (17)	0.4557 (19)	0.4255 (16)
C(39)	−0.3127 (21)	0.5734 (23)	0.3943 (18)
C(40)	−0.2073 (20)	0.6184 (17)	0.3920 (16)
C(41)	−0.1129 (16)	0.5591 (17)	0.4075 (15)

[a] Nitrogen atoms of the pyridine molecules of crystallization were treated as carbon atoms in the refinement. The standard deviations in parentheses refer to the least significant digits.

Results and Discussion

Dissolution of golden $Co_2(HDBAA)_2(py)_4$ in 10% pyridine/90% benzene and crystallization in air result in brilliant red crystals of the binuclear complex in which the ligand molecules are oxidized at the 4-carbons. The yield is essentially quantitative. The infrared spectra in the 2000–400-cm^{-1} region (as KBr pellets) of the original ligand (H_3DBAA), the initial binuclear complex ($Co_2(HDBAA)_2(py)_4$), and the oxidized product ($Co_2(O{=}DBAA)_2(py)_4$) are presented in Figure 2. There are significant, diagnostic differences in the spectra that make identification quite simple. The pentaketone contains a strong, sharp unchelated carbonyl band at 1695 cm^{-1}, which is attributable to the new C=O moiety on each ligand at the 4-carbons.

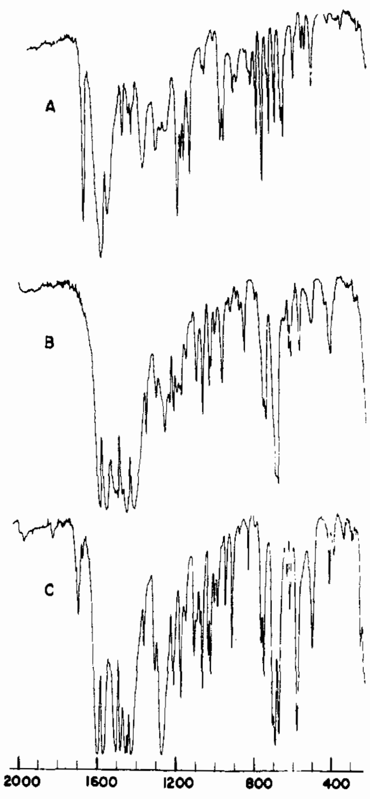

Figure 2. Infrared spectra (KBr pellets) of (A) the uncomplexed ligand, H_3DBAA, (B) $Co_2(HDBAA)_2(py)_4$, and (C) $Co_2(O{=}DBAA)_2(py)_4$.

The structural results for the oxidized product show that the two Co(II) ions are bound to two 1,7-diphenyl-1,3,4,5,7-heptanepentaonato(2−) ligands at the 1,3- and 5,7-positions. Each Co coordination sphere consists of four enolate oxygens from two different $O{=}DBAA^{2-}$ ligands and two axial pyridine nitrogens in typical six-coordinate fashion. This entire array forms a discrete molecule in which the Co(II) ions are 5.37 Å apart. The bond distances and angles in the coordination sphere are quite normal with no unusual distortions. The bond distances and angles associated with the new carbonyl are as expected for an unconjugated carbonyl; i.e., the C–O bond length is 1.22 Å, and the angles about C(4) are 121, 122, and 117°. An ORTEP drawing of the molecule is presented in Figure 1.

The facile oxidation of the ligands in $Co_2(HDBAA)_2$ attests to rather surprising O_2 activation by Co(II) in this β-diketonate-type environment. It is quite normal to expect significant O_2 reactivity with square-planar, low-spin Co(II) as is found in Schiff-base or nitrogen donor macrocyclic type complexes.[4] However, high-spin, pseudooctahedral Co(II) such as is found in β-diketonate complexes is not particularly O_2 sensitive, especially in the absence of anionic species to act as axial ligands for Co(III) products. Such compounds are quite generally stable in solution in the air. Indeed, both the mononuclear Co(II) β-diketonates[15] and the binuclear bis(1,5-diphenyl-1,3,5-pentanetrionato)dicobalt(II)[5] complex may be crystallized from pyridine in the air, yielding the complexes with axial pyridines on the Co(II) ions and with no detectable oxidation of the ligands or of Co(II). Thus, although the Co(II) ions are in very similar environments in all of these compounds (four enolate oxygens and two axial pyridine nitrogens) and all were prepared under very similar conditions, only $Co_2(HDBAA)_2(py)_4$ appears to be O_2 reactive.

It is possible that the 4-carbon in $Co(HDBAA)_2(py)_4$ is particularly susceptible to oxidation under these conditions in which the central position is not occupied by a metal ion and that this accounts for the difference between the Co(II) diketonates and triketonate and the $Co_2(HDBAA)_2(py)_4$ complex. Preliminary

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results for the Cu(II), Ni(II), UO_2^{2+}, Zn^{2+}, and several heterotrinuclear[2,3] complexes of H_3DBAA in which no oxidation is observed lead us to conclude that the oxidation to the 1,3,4,5,7-pentaketonate is metal ion dependent rather than due to unusual ligand susceptibility. The binuclear $Mn_2(DBAA)_2$ complex is also oxidized to what appears to be $Mn_2(O{=}DBAA)_2$,[16] i.e. the compound analogous to $Co_2(O{=}DBAA)_2$. Thus, the oxidation of the ligand does not appear to be simply a function of the 4-carbon reactivity but a selective reaction initiated by specific metal ions.

Acknowledgment is made to the National Science Foundation, Grant CHE 8300251, for support of this research.

Registry No. $Co_2(HDBAA)_2(py)_4$, 94499-12-4; $Co_2(O{=}DBAA)_2(py)_4$·4py, 94499-14-6.

Supplementary Material Available: Complete listings of hydrogen atom parameters and listings of final positional and thermal parameters, bond lengths and angles, and observed and calculated structure factors (14 pages). Ordering information is given on any current masthead page.

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(16) Unpublished results.

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Bromination of Pyrazabole[1]

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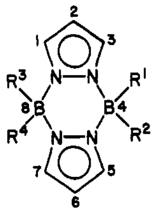
The stepwise B-bromination of pyrazabole with either BBr_3 or Br_2 has been studied. Both 4-bromo- and 4,8-dibromopyrazabole have been isolated and characterized. The former is a thermally unstable species; the latter is formed as a mixture of cis and trans isomers. 4,4,8-Tribromopyrazabole could not be obtained in the pure state but exists in a mixture with the dibromo and tetrabromo derivatives. The X-ray crystal and molecular structures of pyrazabole and 4,4,8,8-tetrabromopyrazabole have been determined. The central B_2N_4 ring of the former exists in boat conformation whereas this same unit of the latter compound is planar. Crystals of pyrazabole, $C_6H_{10}B_2N_4$, belong to space group *Pbca* with $a = 7.645$ (2) Å, $b = 8.391$ (2) Å, $c = 27.372$ (5) Å, and $Z = 8$. 4,4,8,8-Tetrabromopyrazabole, $C_6H_6B_2Br_4N_4$, crystallizes in space group *C*2/*m* with $a = 6.684$ (3) Å, $b = 15.557$ (9) Å, $c = 6.538$ (3) Å, $\beta = 114.45$ (3)°, and $Z = 2$.

Introduction

The reaction of excess elemental bromine with pyrazabole, **1** (R^1 to R^4 = H) = $H_2B(\mu\text{-pz})_2BH_2$ (pz = $N_2C_3H_3$ = pyrazolyl), has been reported to yield 4,4,8,8-tetrabromopyrazabole, $Br_2B(\mu\text{-pz})_2BBr_2$, in a clean reaction.[2] It has also been found that pyrazabole reacts with boron tribromide at temperatures as low as −40 °C to form B-brominated pyrazaboles.[3] Isotopic labeling experiments have shown that this latter process of replacing boron-bonded H by Br does not involve an exchange of boron atoms; i.e., the reaction seems to proceed without opening of the central B_2N_4 ring of the pyrazabole. Furthermore, the existence of the partially brominated species $HBrB(\mu\text{-pz})_2BH_2$, $HBrB(\mu\text{-pz})_2BBrH$, and $Br_2B(\mu\text{-pz})_2BBrH$ was suggested by NMR data. On that basis it seemed reasonable to attempt the isolation and characterization of partially B-brominated pyrazaboles.



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Experimental Section

Elemental analyses were performed by the Schwarzkopf Microanalytical Laboratory, Woodside, NY. Melting points (uncorrected) were determined on a Mel-Temp block. Mass spectral data were obtained from the University of Kentucky Mass Spectrometry Center (recorded on a Perkin-Elmer Hitachi RMU-7 instrument). NMR spectra were recorded on a Varian XL-200 or a Bruker WP-200 instrument. Chemical shift data are given in ppm with positive values indicating downfield shifts from the reference (internal Me_4Si for ^1H and ^{13}C, external Et_2OBF_3 for ^{11}B); coupling constants are given in Hz. Abbreviations: s = singlet, d = doublet, t = triplet, q = quartet, p = quintuplet, m = unresolved multiplet; an asterisk denotes a broad signal. Pyrazabole was prepared by the literature procedure[4] and was recrystallized from methanol. Crystals of 4,4,8,8-tetrabromopyrazabole were obtained from a solution in CH_2Br_2. Crystal data were obtained on a Syntex P3 au-

Table I. Summary of Crystallographic Data and Data Collection Procedures[a]

compd	pyrazabole	4,4,8,8-tetrabromopyrazabole
formula	$C_6H_{10}B_2N_4$	$C_6H_6B_4Br_4N_4$
fw	159.80	475.38
cryst size, mm	0.30 × 0.28 × 0.42	0.30 × 0.22 × 0.35
space group	*Pbca*	*C*2/*m*
a, Å	7.645 (2)	6.684 (3)
b, Å	8.391 (2)	15.557 (9)
c, Å	27.371 (5)	6.538 (3)
α, deg	90	90
β, deg	90	114.45 (3)
γ, deg	90	90
Z	8	2
V, Å^3	1755.9 (1)	618.9 (5)
d_{calcd}, g/cm^3	1.21	2.55
μ, cm^{-1}	0.71	128.6
F(000)	671.76	439.89
2θ, deg	2–45	2–52
scan speed, deg/min	1.2–29.3	2–29.3
scan width, deg	0.9	0.9
total no. of reflcns	1446	1073
no. of unique reflcns	1385	1073
no. of variables used	149	44
R	0.039	0.064
R_w	0.0377	
g	0.0003	

[a] In this and all subsequent tables esd's are given in parentheses.

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(1) (a) Boron–Nitrogen Compounds. 100 (K.N.). Part 99: Niedenzu, K.; Niedenzu, P. M. *Inorg. Chem.* **1984**, *23*, 3713. (b) Contributions to the Chemistry of Boron. 147 (H.N.). Part 146: Kumpfmüller, F.; Nölle, D.; Nöth, H.; Pommerening, H.; Staudigl, R. *Chem. Ber.*, in press.
(2) Trofimenko, S. *J. Am. Chem. Soc.* **1967**, *89*, 4948.
(3) Niedenzu, K.; Nöth, H. *Chem. Ber.* **1983**, *116*, 1132.
(4) Trofimenko, S. *J. Am. Chem. Soc.* **1967**, *89*, 3165.