Tetrameric Cations Derived from *o*-Aminobenzaldehyde and Their Utility in the Synthesis of Complexes of a Tetraazaannulene[1]

JOHN S. SKURATOWICZ, IAN L. MADDEN, and DARYLE H. BUSCH*

o-Aminobenzaldehyde is known to form a variety of macrocyclic oligomeric ligands having a rich and significant coordination chemistry. This report describes a series of diacid salts of a related tetramer of *o*-aminobenzaldehyde, $C_{28}H_{20}N_4(HX)_2$, abbreviated $TAAB(HX)_2$, $X = BF_4$, ClO_4, Br, Cl, HSO_4, and CF_3SO_3. These salts are excellent reagents for the preparation of the complexes of the Schiff base ligand TAAB. The structure of the tetrameric cation has been assigned and is properly named 4b,5,15b,16-tetrahydrodibenzo[3,4:7,8][1,5]diazocino[2,1-*b*:6,5-*b*]diquinazoline-11,22-diium ion. Reactions of $TAAB(HX)_2$ with metal acetates yield the known TAAB complexes and some complexes not previously prepared. Partial hydrogenation of $TAAB(HX)_2$ produces isomeric substances H_4TAAB which have distinctive ligand properties.

Introduction

A number of complexes of the 16-membered macrocyclic ligand TAAB (I) have resisted synthesis despite the fact that

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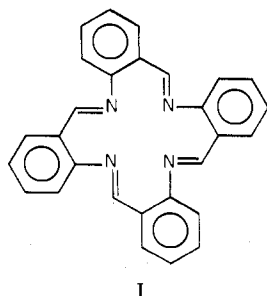
three distinct routes are known for the preparation of complexes with this ligand. The known methods involve the template reaction of *o*-aminobenzaldehyde,[2–4] rearrangement of the trimer or tetramer of aminobenzaldehyde,[5] and ligand transfer from Zn(TAAB)ZnCl$_4$.[6,7] Despite a number of earlier attempts, satisfactory results with the metals iron(II) and rhodium(III) had not been achieved. The facile reaction of the Fe(II)–TAAB complexes (formed by the template reaction) with water and oxygen has yielded the stable iron(III) oxo-bridged dimer,[8] Fe(TAAB)$_2$O^{4+}. Rhodium(III) ion is much too inert to participate in a template reaction. Related difficulties were encountered for these two metals using the second method. Success was achieved by Katovic in the synthesis of Pd(TAAB)$^{2+}$ by the ligand-exchange reaction of route 3;[8] this method, however, gives poor results when applied to iron(II).[7]

Because of the importance of iron in naturally occurring macrocycles and the sparsity of studies with metals of the second transition series, we have reexamined the macrocyclic ligand systems derived from *o*-aminobenzaldehyde in order to develop a useful route to these complexes.

o-Aminobenzaldehyde undergoes self-condensation yielding several products, depending on the conditions. Storage of the base for a long time has been shown[9] to yield a tricyclic bis-anhydro trimer (II) and a tricyclic trisanhydro tetramer (III).

II   III
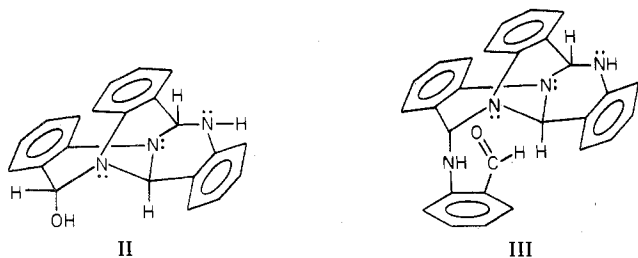
The structures of these condensates have been confirmed by McGeachin.[10] The tricyclic trimer (II) is exclusively and

rapidly formed by the action of weak or dilute acids.[11,12] If a strong or mineral acid is used, a red diacid salt of *o*-aminobenzaldehyde is formed, which may be readily converted by water to the tricyclic trisanhydro tetramer (II).[9] The condensation of *o*-aminobenzaldehyde in the presence of metal ions gives radically different products, metal complexes possessing macrocyclic ligands with three[2,13] or four Schiff base linkages,[2–7] which have usually been denoted by the abbreviations TRI (IV) and TAAB (I), respectively.[14]

IV
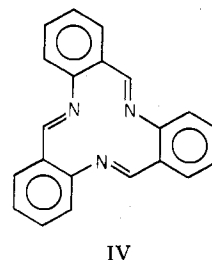
Albert and Yamamoto[15] proposed a bicyclic hydrogen-bonded structure containing an alcohol group for the red dihydrochloride salt of *o*-aminobenzaldehyde (V) on the basis

V
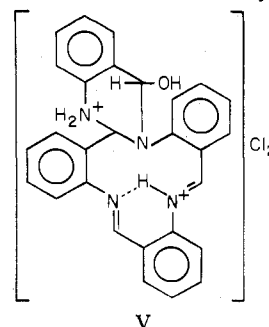
of the empirical formula $C_{28}H_{22}N_4O \cdot 2HCl$ and infrared, electronic, and nuclear magnetic resonance spectra.

We report here that the red diacid salt of *o*-aminobenzaldehyde contains 4b,5,15b,16-tetrahydrodibenzo[3,4:7,8]-[1,5]diazocino[2,1-*b*:6,5-*b*]diquinazoline-11,22-diium ions (VI).

VI
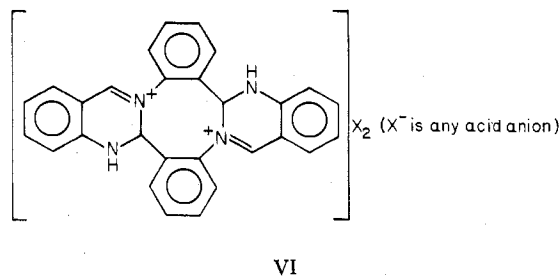
This conclusion is based on chemical and physical evidence and supported by the preliminary x-ray results on the red

trifluoromethylsulfonate salt of *o*-aminobenzaldehyde.[16] The diacid salts undergo facile reaction with metal acetates to yield the familiar metal–TAAB complexes. In addition, sodium borohydride reduces the diacid salts to a new partially saturated ligand, H₄TAAB (VII). Metal complexes of this new
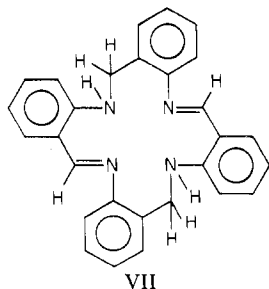
VII

macrocyclic ligand are discussed elsewhere.[17]

Experimental Section

Materials. *o*-Aminobenzaldehyde was prepared from *o*-nitrobenzaldehyde (Aldrich, Milwaukee, Wis.) by reduction with ferrous sulfate, according to Smith and Opie.[18] All other chemicals were obtained commercially and were of reagent grade.

Reaction of *o*-Aminobenzaldehyde with HBF₄. Forty grams of crude *o*-aminobenzaldehyde was dissolved in 100 mL of acetonitrile. The yellow solution was treated with anhydrous sodium sulfate and filtered over anhydrous sodium sulfate. Twenty milliliters of 48% tetrafluoroboric acid was slowly added to the filtrate and the resulting red solution was set aside for 8 h during which time it deposited red crystals of TAAB(HBF₄)₂. A total yield of 30 g (~70%) was obtained: 14 g from the initial crystallization and the remainder from the filtrate by further addition of HBF₄ and ether. The crystals were washed with a 1:1 ether–acetonitrile mixture, followed by anhydrous ether. The salt was recrystallized from warm acetonitrile by addition of anhydrous ether. Anal. Calcd for $C_{28}H_{22}N_4B_2F_8$: C, 57.18; H, 3.77; N, 9.52. Found: C, 57.32; H, 3.80; N, 9.57. Infrared spectrum: ν_{NH} 3340, $\nu_{C=C}$ 1630, $\nu_{C=N}$ 1563, ν_{BF_4} 1140, and $\delta_{C_6H_4}$ 780, 768 cm⁻¹, in Nujol. Mass spectrum: highest mass peak at *m/e* 412 which is P – 2HBF₄; the parent peak was not observed. Electronic spectrum: ν_{max}(CH₃CN) 22 000 cm⁻¹ (ε 590).

Reaction of *o*-Aminobenzaldehyde with HBr. The dihydrobromide salt was prepared in a similar manner to give TAAB(HBr)₂ as the monohydrate. Anal. Calcd for $C_{28}H_{22}N_4Br_2\cdot H_2O$: C, 56.77; H, 4.08; N, 9.46; Br, 26.98; O, 2.79. Found: C, 56.82; H, 4.14; N, 9.09; Br, 27.20; O, 3.46. Infrared spectrum: ν_{OH} 3520, ν_{NH} 3380, $\nu_{C=C}$ 1625, $\nu_{C=N}$ 1555, and $\delta_{C_6H_4}$ 787, 768 cm⁻¹, in Nujol. Mass spectrum: base peak at *m/e* 412 which is P – 2HBr, H₂O. NMR spectrum in CF₃CO₂H vs. TMF: a complex multiplet at 7.00 ppm and another more intense multiplet at 7.50 ppm, 2 OH; and a singlet at 9.18 ppm, 2 H.

Reaction of *o*-Aminobenzaldehyde with HClO₄. When perchloric acid was used, the TAAB(HClO₄)₂ salt was obtained in a 60% yield. *Caution!* Solutions of HClO₄ in organic solvents constitute an explosion hazard! Anal. Calcd for $C_{28}H_{22}N_4Cl_2O_8$: C, 54.82; H, 3.61; N, 9.13. Found: C, 54.72; H, 3.54; N, 9.30. Infrared spectrum: ν_{NH} 3320, $\nu_{C=C}$ 1625, $\nu_{C=N}$ 1560, ν_{ClO_4} 1105, and $\delta_{C_6H_4}$ 790, 771 cm⁻¹, in Nujol.

Reaction of *o*-Aminobenzaldehyde with HCF₃SO₃. In the reaction of trifluoromethylsulfonic acid with *o*-aminobenzaldehyde, dissolved in the minimum amount of acetonitrile and dehydrated as above, the strongly acidic solution was dropwise diluted with water before crystallization occurred. The yield of the red sulfonate salt was about 80%. The salt was recrystallized from warm acetonitrile, containing a few drops of the acid, by addition of ether. Anal. Calcd for $C_{30}H_{22}N_4F_6O_6S_2$: C, 50.56; H, 3.11; N, 7.86. Found: C, 50.71; H, 3.11; N, 7.81. Infrared spectrum: ν_{NH} 3280, $\nu_{C=C}$ 1630, $\nu_{C=N}$ 1560, ν_{SO_2} 1270, 1034, and $\delta_{C_6H_4}$ 778 cm⁻¹, in Nujol. Mass spectrum: base peak at *m/e* 412 which is parent less 2 mol of trifluoromethylsulfonic acid; again, the parent peak was not observed. NMR spectrum in CD₃CN vs. TMS: two complex multiplets, centered at 7.00 and 7.55 ppm accounted for 2 OH, with a singlet at 8.98 ppm integrating for two protons.

Reaction of *o*-Aminobenzaldehyde with H₂SO₄. Five grams of the base was treated with 20 mL of 9 M sulfonic acid. An equal volume

of distilled water was added, and upon scratching the sides, TAAB(H₂SO₄)₂ was deposited profusely. The crystals were collected, washed with ethanol–ether solutions (1:1 ratio) and then ether, and air-dried; yield ~50%. Anal. Calcd for $C_{28}H_{24}N_4S_2O_8$: C, 55.40; H, 4.00; N, 9.25. Found: C, 54.95; H, 4.07; N, 8.96. Infrared spectrum: ν_{NH} 3315, $\nu_{C=C}$ 1620, $\nu_{C=N}$ 1569, ν_{SO_4} 1061, and $\delta_{C_6H_4}$ 780, 770 cm⁻¹, in Nujol. Mass spectrum: base at *m/e* 412, corresponding to TAAB⁺ or $C_{28}H_{20}N_4^+$ with no parent peak observed.

Reaction of *o*-Aminobenzaldehyde with HCl. The dihydrochloride salt was prepared in a manner similar to the H₂SO₄ salt. The product is a lattice compound of complicated stoichiometry. Anal. Calcd for TAAB(HCl)₂.₅(H₂O)₃.₅ or $C_{28}H_{29.5}N_4Cl_{2.5}O_{3.5}$: C, 59.34; H, 4.27; N, 9.89; Cl, 15.64. Found: C, 58.27; H, 5.05; N, 9.59; Cl, 15.26. A sample was ground and heated to 130–135 °C for 24 h in vacuo. Analysis for the dried sample gave TAAB(HCl)₂(H₂O)₂ or $C_{28}H_{22}N_4Cl_2\cdot 2H_2O$. Anal. Calcd: C, 64.50; H, 5.02; N, 10.74; Cl, 13.60. Found: C, 64.36; H, 5.11; N, 10.57; Cl, 12.44. Infrared spectrum: ν_{NH} 3385, $\nu_{C=C}$ 1625, $\nu_{C=N}$ 1562, $\delta_{C_6H_4}$ 770, 758 cm⁻¹. Mass spectrum: base at *m/e* 412 which is parent less the HCl and H₂O molecules. Electronic spectrum in acetonitrile: ν_{max} 22 000 (ε 530), 32 390 (2540), 41 500 (3460 sh), 44 670 cm⁻¹ (10 310 sh).

Reaction of Diacid Salts of *o*-Aminobenzaldehyde with Metal Acetates. The diacid salt, TAAB(HBF₄)₂ (9.60 g, 1 mmol), was ground and suspended in 200 mL of absolute ethanol. Fifty milliliters of hot ethanol solution containing 0.50 g of dissolved Ni(CH₃CO₂)₂·4H₂O, (2 mmol) was added with stirring. The solution changed color from the orange-red of the diacid salt to the purple-red of the complex and within 15 min of the initial reflux the NiTAAB(BF₄)₂ complex began to crystallize. Anal. Calcd for $C_{28}H_{20}N_4B_2F_8Ni$: C, 52.30; H, 3.12; N, 8.70. Found: C, 52.01; H, 3.24; N, 8.77.

The reaction proceeds according to

$$M(CH_3CO_2)_2 \cdot nH_2O + TAAB(HX)_2 \xrightarrow{CH_3CN} M(TAAB)X_2$$

$$+ 2CH_3CO_2H + nH_2O \qquad (1)$$
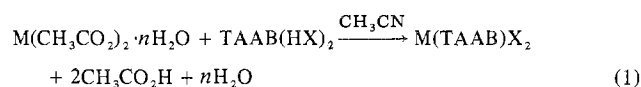
for metals such as cobalt(II), copper(II), and iron(II). In the case of iron(II), the complex is prepared in an oxygen- and water-free environment to get [Fe(TAAB)(CH₃CN)₂](BF₄)₂, when using TAAB(HBF₄)₂. Anal. Calcd for $C_{32}H_{26}N_6B_2F_8Fe$: C, 53.08; H, 3.62; N, 11.61; Fe, 7.71. Found: C, 51.72; H, 3.76; N, 11.54; Fe, 7.11. Recrystallization of the complex from pyridine affords [Fe(TAAB)(C₅H₅N)₂](BF₄)₂. Anal. Calcd for $C_{38}H_{30}N_6B_2F_8Fe$: C, 57.04; H, 3.78; N, 10.50. Found: C, 57.21; H, 3.97; N, 10.70.

In the reaction with rhodium trichloride, a little less than 1 mmol (0.20 g) of rhodium trichloride trihydrate was maintained at reflux in 25 mL of acetonitrile until the color changed to orange-yellow. TAAB(HClO₄)₂, 0.5 g, dissolved in 25 mL of acetonitrile was added to the above solution and reflux was continued for 50 h. The solution was cooled and filtered. Addition of ether to the filtrate gave the desired product, which was recrystallized from acetonitrile containing a small amount of perchloric acid, by addition of ether. *Caution!* Solutions of HClO₄ in organic solvents constitute an explosion hazard! Anal. Calcd for [Rh(TAAB)(CH₃CN)₂](ClO₄)₃·H₂O or $C_{32}H_{28}N_6Cl_3O_{13}Rh$: C, 42.06; H, 3.09; N, 9.21. Found: C, 41.62; H, 3.30; N, 9.69.

Partial Hydrogenation of the Diacid Salt with Sodium Borohydride. Five grams of finely pulverized TAAB(HBF₄)₂ salt was suspended in 50 mL of methanol. The slurry was stirred vigorously and a total of 1.0 g of NaBH₄ was added in small portions. The reaction was considered to be complete when the reactant TAAB(HBF₄)₂ had completely dissolved, at which time an additional 0.1 g of NaBH₄ solid was added. The yellow solid was collected, washed twice with methanol, and dried. The yellow solid was extracted with warm chloroform until the filtrates were colorless. The volume of the resulting solution was reduced to half its initial value and an equal portion of methanol was added. This produced 2.55 g of the finely crystalline yellow product H₄TAAB. Similar treatment of the original filtrate gave an additional 0.30 g of H₄TAAB for a total of 2.85 g or approximately 80% yield. Anal. Calcd for H₄TAAB or $C_{28}H_{24}N_4$: C, 80.74; H, 5.81; N, 13.45. Found: C, 80.26; H, 5.61; N, 13.56. Infrared spectrum: ν_{NH} 3260, $\nu_{C=C}$ 1620, $\nu_{C=N}$ 1525, and $\delta_{C_6H_4}$ 764, 755 cm⁻¹. Electronic spectrum in chloroform: ν_{max} 26 300 cm⁻¹ (ε 18 000). NMR spectrum in CDCl₃ vs. TMS: 2 H at 9.82 ppm, broad singlet; 2 H at 8.30 ppm, sharp singlet; 16 H at 7.16 and 6.74 ppm, multiplets; 4 H at 4.47 ppm, broad doublet, J = 6 Hz. Mass spectrum of yellow H₄TAAB gave a parent peak for $C_{28}H_{24}N_4^+$ at *m/e* 416.

Table I. Comparison of Some Infrared Absorption Bands for the Diacid Salts and Other o-Aminobenzaldehyde Derivatives (cm⁻¹)

	ν_{NH} m[a]	$\nu_{C=N}$ vs	$\nu_{C=C}$ ring modes				CH bending vs
			I vs	II w	III m	IV s	
TAAB(HBF₄)₂	3340	1552	1622	1595	1498	1478	785, 773
TAAB(HBr)₂·H₂O	3380	1555	1625	1590	1480	1470	787, 768
TAAB(HClO₄)₂	3320	1560	1625	1595	1496	1474	790, 771
TAAB(CF₃SO₃H)₂	3280	1560	1630	1596	1500	1478	778 b
TAAB(H₂SO₄)₂	3315	1569	1620	1600	1500	1480	780, 770
TAAB(HCl)₂·2H₂O	3385	1560	1625	1594	1495	1478	770, 758
Trimer (I)	3302		1605	1575	1478	1455	765

[a] Key: m, medium; s, sharp; vs, very sharp; w, weak; b, broad.

A white isomer of the H₄TAAB ligand has been prepared by repeated recrystallizations (as many as three times) from hot acetonitrile of a sample of H₄TAAB. Anal. Calcd for H₄TAAB or C₂₈H₂₄N₄: C, 80.74; H, 5.81; N, 13.45. Found: C, 80.52; H, 6.01; N, 13.48. Infrared spectrum: ν_{NH} 3518, 3400, $\nu_{C=C}$ 1615, and $\delta_{C_6H_4}$ 760 cm⁻¹. NMR spectrum in CDCl₃ vs. TMS: 16 H in the aromatic region at 7.00 ppm, 8 H in an array of singlets centered at 4.64 ppm. The mass spectrum of white H₄TAAB ligand shows a base peak at m/e 310 (P − 106) and a parent peak at m/e 416, 60% as intense as the base peak.

Reduction of Yellow H₄TAAB. Yellow H₄TAAB (1.0 g) was suspended in 100 mL of anhydrous ether in a three-necked 500-mL flask, and argon was passed through the solution for 10 min. An ether dispersion of lithium aluminum hydride was added slowly in two portions (initial 0.35 g and final 0.20 g) with stirring. The excess hydride was neutralized with ethyl acetate added in four portions of 25 mL each to the reaction mixture. Thirty milliliters of water was added, slowly, to produce a milky white aqueous layer with a yellow organic layer above it. The volume of the organic layer was reduced to about 40 mL, and after thorough drying over anhydrous sodium sulfate, the solution on cooling gave a pale yellow precipitate of H₈TAAB. The crude material was recrystallized from chloroform by addition of methanol. Anal. Calcd for H₈TAAB or C₂₈H₂₈N₄: C, 80.00; H, 6.70; N, 13.30. Found: C, 79.43; H, 6.46; N, 13.35. Infrared spectrum: ν_{NH} 3370, $\nu_{C=C}$ 1605, and $\delta_{C_6H_4}$ 756 cm⁻¹. The mass spectrum of H₈TAAB shows the parent C₂₈H₂₈N₄⁺ at m/e 420, but the most intense peak is at m/e 209, (P − 2)/2. A nickel complex prepared with this H₈TAAB ligand has an infrared spectrum identical with that of a complex prepared by a different route.[19]

Physical Measurements. A Perkin-Elmer 337 infrared spectrophotometer was used to obtain the spectra of the ligands and complexes, using both Nujol and KBr techniques. A Cary 14R recording spectrophotometer was used to obtain solution spectra in 1-cm quartz cells. Proton nuclear resonance spectra were obtained using a JEOL JNM-MZ 100 instrument of the Japan Electron Optical Laboratory, Co., Ltd., Tokyo, Japan. Most of the samples were prepared using deuterated solvents with TMS as the internal standard. Mass spectra were kindly prepared by Mr. C. R. Weisenberger of OSU on the AEI MS-9 spectrometer. All analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn., or by Chemalytics, Tempe, Ariz.

Results and Discussion

There are four synthetic routes to the diacid salts of o-aminobenzaldehyde (Scheme I) that are reported here. The most convenient and efficient involves the neutralization of the base (dissolved in acetonitrile or suspended in water) with the desired acid. Using this method, the following anhydrous salts have been prepared: TAAB(HBF₄)₂, TAAB(HClO₄)₂, TAAB(H₂SO₄)₂, and TAAB(CF₃SO₃H)₂. The hydrated salts TAAB(HBr)₂·H₂O and TAAB(HCl)₂·2H₂O have also been prepared in this way. A sample of TAAB(DBF₄)₂ was isolated from a solution of o-aminobenzaldehyde and CF₃SO₃D (from D₂O and (CF₃SO₃)₂O) on the addition of solid NaBF₄. All of these salts have been identified as condensates of o-aminobenzaldehyde containing four units of the base less four molecules of water and are formulated as [C₂₈H₂₂N₄²⁺]X⁻₂ or simply TAAB(HX)₂.

The infrared spectra of the hydrated and anhydrous diacid salts are identical except for anion and water vibrational modes, indicating the presence of the same organic cation

Scheme I. Synthetic Routes to TAAB Diacid Salts, Where X⁻ = BF₄⁻, Br⁻, Cl⁻, ClO₄⁻, HSO₄⁻, and CF₃SO₃⁻
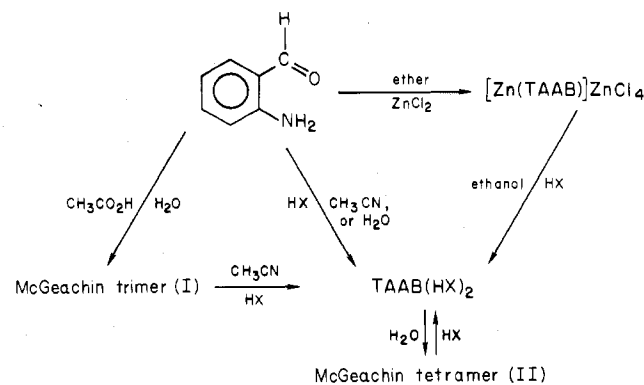
throughout the series. The frequency of the NH stretching mode, however, appears to be consistently higher for the hydrated salts (Table I). The ring vibrations associated with the benzene rings are found at 1625 ± 5, 1595 ± 5, 1495 ± 5, and 1475 ± 5 cm⁻¹ for the series of diacid salts. The strong band at 1555 ± 5 cm⁻¹ is assigned to C=N stretching mode. No such vibration occurs for the neutral bisanhydro trimer (II) and trisanhydro tetramer (III) indicating that their structures are not closely related to the structure of the diacid salt. This value (1555 cm⁻¹) is intermediate between those for the C=N vibration of metal TAAB complexes at 1570 cm⁻¹ and those occurring at 1530 cm⁻¹ for derivatives of the TAAB complexes which have suffered nucleophilic addition of such bases as RO⁻ or R₂N⁻ for two of their C=N groups.[20] From this it is suggested that the diacid salts possess conjugated imine bonds that are less delocalized than is true of the nucleophilic adducts.[20]

The electronic spectra of the anhydrous and hydrated diacid salts are identical. Both exhibit a long-wavelength maximum at 22 000 cm⁻¹, which suggests the presence of a conjugated azomethinium group −CH=N⁺<.[15]

The comparison of the mass spectral fragmentation pattern of the major isotope envelopes (10% or greater intensity of the parent peak) of the diacid salt series (Table II) confirms the conclusion suggested by the electronic and infrared data that the two types of salts contain the same organic moiety. The elements of water in the formulation of the hydrobromide and hydrochloride salts are present as lattice water molecules and not as part of an alcohol derivative as was suggested for the HCl salt.[15] Dehydration experiments substantiate this interpretation. The dihydrochloride TAAB(HCl)₂.₅·3.5H₂O, on dehydration at 130 °C for 24 h, becomes TAAB(HCl)₂·2H₂O, whereas the dihydrobromide TAAB(HBr)₂·H₂O becomes TAAB(HBr)₂ on dehydration. An infrared spectrum of the anhydrous dihydrobromide showed a reappearance of a band at 3520 cm⁻¹ due to H₂O on exposure of the sample to the moisture of the air.

The properties of the salts suggest a structure different from that of the neutral McGeachin trimer (II) or the tetramer (III) of o-aminobenzaldehyde and from that of the TAAB ligand

Table II. Mass Spectral Data for TAAB(HX)$_2 \cdot n$H$_2$O, Expressed as Percent of Base m/e of 412

m/e	HBr	HBF$_4$	HCl	H$_2$SO$_4$	CF$_3$SO$_3$H
414	24.1	16.2	9.7	20.5	15.4
413	34.8	32.5	31.6	37.7	31.5
412	100.0	100.0	100.0	100.0	100.0
411	56.1	56.9	51.6	60.0	57.7
320	20.3	12.2	8.8	30.5	
308	18.9	13.8	53.5		83.1
305				38.9	
295				38.9	
294	26.6	17.9			
293	72.3	48.9	17.2		37.7
283	56.1	78.9	103.2		80.7
207	20.5	19.5	20.4		
206	37.2	37.3	49.9		73.0
205	24.1	33.3	46.9		50.0
192	16.3	11.7	9.8		17.2

(I). Further, it has just been shown that the species is not an alcohol derivative (V). A strong clue to the structure is found in the behavior of anthranilic acid which has been shown[19] to undergo a dehydrocyclization, to yield the tricyclic tetramer having structure VIII. It is reasonable to expect the tetrameric
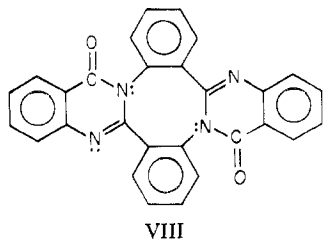

VIII

cation produced by the reaction of *o*-aminobenzaldehyde with mineral acids to have a structure similar to VIII. The assigned structure is VI.

The proton NMR spectra of the diacid salts may be rationalized in terms of VI. They show a sharp singlet at about 9 ppm from TMS due to two azomethine protons[10,15] and complex multiplets centered at 7 and 7.5 ppm for 20 protons, of which 16 may be assigned to the ortho-disubstituted benzene protons.[22] An NMR spectrum of TAAB(DBF$_4$)$_2$ shows only 18 protons in the aromatic region, indicating that the NH protons of the diacid salts absorb in this same region. The two protons not previously assigned must be those associated with the R$_3$–CH moieties (see structure VI). Such protons commonly absorb in the range between 5.35 and 5.65 ppm[10] but the greater deshielding due to ring currents in the diacid salt (VI) may position them downfield, essentially in the aromatic region. This physical evidence is consistent with the proposed tricyclic structure (VI) for the diacid salts in that there are two NH groups, two azomethine groups, and four anhydro units derived from *o*-aminobenzaldehyde. The chemical evidence is also consistent with that structure.

Study of the borohydride and borodeuteride reduction products of the diacid salts shows that attack occurs only at the azomethine carbon. The reduced neutral ligand H$_4$TAAB, C$_{28}$H$_{24}$N$_4$, assumes an open 16-membered ring structure (VII), possessing two C=N imine bonds which are not subject to reduction by NaBH$_4$. H$_4$TAAB (VII) can be made to undergo internal cyclization to yield a tricyclic isomer form (IX), which is analogous to the proposed structure (VI) for the diacid salts (vide infra).

The reaction of metal acetates with diacid salts TAAB-(HX)$_2$ yields exclusively the metal TAAB complexes. In the case of nickel acetate, no trace of side products (such as NiTRI^{2+}) was found, indicating that complexation involves only bond breaking in the inner ring, with the outer 16-


IX
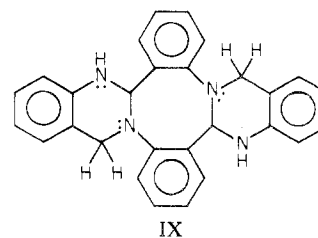
membered ring remaining intact. The Experimental Section reveals that these diacid salts may be used to synthesize the complexes of TAAB with Fe^{II} and Rh^{III}. These are appropriately the subject of a separate report.[17]

Additional evidence for the tricyclic structure of the diacid salt comes from an x-ray examination of a single crystal of TAAB(CF$_3$SO$_3$H)$_2$ by Yates and Corfield.[15] The diacid salt was found to be disordered which prevented differentiation between =N$^+$<, –NH, and =CH groups. However, the results clearly showed the polycyclic structure and the saddlelike arrangement of the four six-membered rings that surround the eight-membered inner ring in VI.

The reduction products of the diacid salts are of interest in their own right since they are potentially new macrocyclic ligands. The yellow H$_4$TAAB ligand has essentially the same structure free as when it is complexed to a metal ion.[17] The infrared spectrum of yellow H$_4$TAAB shows a ν_{NH} absorption at 3260 cm^{-1} and $\nu_{C=N}$ at 1525 cm^{-1} (consistent with structure VIII). The proton NMR spectrum in CDCl$_3$ vs. TMS shows the expected NH protons at 9.82 ppm. The imine protons display a singlet at 8.30 ppm, while the 16-membered aromatic protons produce complex multiplets at 7.16 and 6.74 ppm. A doublet ($J = 6$ Hz) at 4.47 ppm is due to the four methylene protons, presumably split by the NH protons. In the NMR spectrum of D$_4$TAAB (prepared from TAAB(HBF$_4$)$_2$ and NaBD$_4$, followed by recrystallization from CHCl$_3$ by addition of CH$_3$OD), the methylene doublet collapsed to a singlet at 4.47 ppm, but a new singlet appeared at 4.00 ppm. The unequal intensities of the two singlets suggest different concentrations of the cis and trans deuteriomethylene isomers. These facts, in addition to elemental analysis and mass spectrum, are consistent with the 16-membered ring structure (VII) proposed for yellow H$_4$TAAB ligand.

A white thermodynamically more stable isomer of the yellow H$_4$TAAB ligand has been isolated. Its white color and the absence of the –C=N– absorption in its infrared spectrum is consistent with structure IX. The proton NMR spectrum of white H$_4$TAAB shows a resonance due to 16 protons in the aromatic region at 7.00 ppm and a resonance due to eight protons gives an array of sharp bands centered at 4.64 ppm. No signals are observed downfield from the aromatic region and this requires that there be no imine groups in the white isomer (consistent with IX). Both isomers give the same metal complex with nickel ions, namely, [NiH$_4$TAAB-(CH$_3$CN)$_2$](ClO$_4$)$_2$, which means that ring opening in IX occurs rather easily during the course of the complexation reaction.

The imine bonds of the yellow isomers are easily reduced by LiAlH$_4$ or hydrogen gas with PtO$_2$ as a catalyst. The former method is preferred because it is quicker and gives greater yields. The reduction leads to the isolation of the fully saturated free H$_8$TAAB ligand (X) for the first time. This ligand was previously reported in its Ni^{2+} complex.[19] The infrared spectrum of H$_8$TAAB shows an N–H stretching band at 3370 cm^{-1}, somewhat higher in energy than the NH absorption found in H$_4$TAAB. Full reduction is evidenced by the absence of imine absorptions around 1560 cm^{-1}. The ring modes of H$_8$TAAB are seen at 1605, 1582, 1505–1485, and 1435 cm^{-1}, with the out-of-plane deformation of the substituted benzene occurring at 756 cm^{-1}. The mass spectrum shows a

X
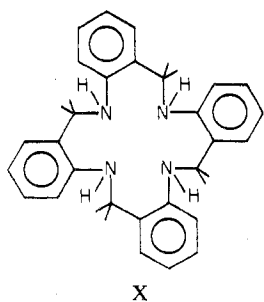
parent ion at m/e 420, which is the mass number for $C_{28}H_{22}N_4^+$ or H_8TAAB^+ cation. No nonintegral mass number absorptions (which arise when a species is doubly charged and has an odd mass number) are observed in the mass spectrum of H_8TAAB. This is in contrast to the behavior of the diacid salts and the isomers of H_4TAAB, where numerous nonintegral absorptions are seen, beginning with the m/e 206 (B/2) isotope envelope. The phenomenon can be rationalized if it is assumed that π electrons of imine bonds are most susceptible to scattering. Electron loss from two (or more) such bonds (leading to heteroatom cation stabilization) would lead to multicharged species.

A nickel complex of the H_8TAAB ligand was prepared and the infrared spectrum of the product contains no $\nu_{C=N}$ absorption and is congruent with that of a sample of NiH_8TAAB^{2+} prepared by other means.[19]

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Registry No. TAAB(HBF$_4$)$_2$, 62609-18-1; TAAB(HBr)$_2$, 62637-56-3; TAAB(HClO$_4$)$_2$, 62609-19-2; TAAB(CF$_3$SO$_3$H)$_2$,

62609-20-5; TAAB(H$_2$SO$_4$)$_2$, 62609-21-6; TAAB(HCl)$_2$, 62609-22-7; trimer (II), 25334-63-8; o-aminobenzaldehyde, 529-23-7; HBF$_4$, 16872-11-0; HBr, 10035-10-6; HClO$_4$, 7601-90-3; HCF$_3$SO$_3$, 1493-13-6; H$_2$SO$_4$, 7664-93-9; HCl, 7647-01-0; NiTAAB(BF$_4$)$_2$, 14286-44-3; [Fe(TAAB)(CH$_3$CN)$_2$](BF$_4$)$_2$, 62637-62-1; [Fe(TAAB)(C$_5$H$_5$N)$_2$](BF$_4$)$_2$, 62637-64-3; [Rh(TAAB)(CH$_3$CN)$_2$]-(ClO$_4$)$_3$, 62637-66-5; H$_4$TAAB (yellow isomer), 62609-23-8; H$_4$TAAB (white isomer), 62609-24-9; H$_8$TAAB, 62609-25-0.

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Quinone Adducts of Transition Metal Nitrosyl Complexes

MAURO GHEDINI, GIULIANO DOLCETTI,* BRUNO GIOVANNITTI, and GIANFRANCO DENTI

The results of the interaction of complexes of the type M(NO)(CH$_3$CN)$_2$L$_2^{2+}$ (M = Rh, Ir; L = P(C$_6$H$_5$)$_3$, As(C$_6$H$_5$)$_3$) with o-quinones and o-catechols in alcohol or diethyl ether are reported. The compounds obtained are pentacoordinate and tetracoordinate nitrosyl catecholato complexes, which differ for the nitrosyl bonding mode and the metal oxidation state. The tetracoordinate complex achieves pentacoordination by reversible addition of triphenylphosphine. The individual reaction steps have been studied in order to elucidate the metal complex and o-quinone chemical behavior. An alkoxide intermediate complex has been isolated in the iridium case and its chemistry studied. A parallel study with iridium arsine complexes has been done to establish the neutral ligand influence on the reaction. The simultaneous presence of the two ligands nitrosyl and quinone, for which different coordination modes are possible, confers upon the complexes a particular flexibility.

Introduction

Transition metal complexes of o-benzoquinones have been known for many years, but only recently have significant steps been taken to understand the nature of the metal–quinone bond. Three different coordination modes are possible for o-benzoquinones, differing in the formal oxidation state of the ligand

I   II   III
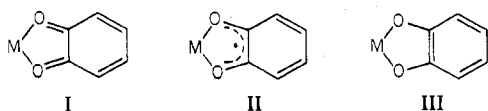
The relative importance of the configurations I and III should depend on the basicity of the metal and on the oxidizing ability of the quinone itself. Among the earliest reports of o-benzoquinone coordination are examples of complexes with metals of low basicity.[1] The weaker oxidants 9,10-phenanthrenequinone and 1,2-naphthoquinone react with difficulty and often form complexes with metals (i.e., Zn(II), Mo(IV)) for which the olefin coordination is unlikely; these complexes probably contain unreduced quinone ligands.[2] Addition reactions of o-benzoquinones with a variety of nucleophic group 8 metal complexes with d^8 and d^{10} electronic metal configuration have been studied.[3–10] On coordination the qui-