

Table III. Fragment Orbitals in the E_yE_y Conformation

$[\text{MoN}_4]_{E_yE_y}$	$[\text{O}_2]$	n	
z^2	$(\sigma_g^u + \sigma_g^l); (\pi_u^{u\parallel} - \pi_u^{l\parallel})$	4	A_g
xy	$(\pi_g^{u\perp} + \pi_g^{l\perp})$	2	B_{1g}
xz	$(\pi_u^{u\perp} - \pi_u^{l\perp})$	2	B_{2g}
yz	$(\pi_g^{u\parallel} + \pi_g^{l\parallel})$	2	B_{3g}
	$(\pi_g^{u\perp} - \pi_g^{l\perp})$	2	A_u
	$(\sigma_g^u - \sigma_g^l); (\pi_u^{u\parallel} + \pi_u^{l\parallel})$	4	B_{1u}
	$(\pi_g^{u\parallel} - \pi_g^{l\parallel})$	2	B_{2u}
	$(\pi_u^{u\perp} + \pi_u^{l\perp})$	2	B_{3u}

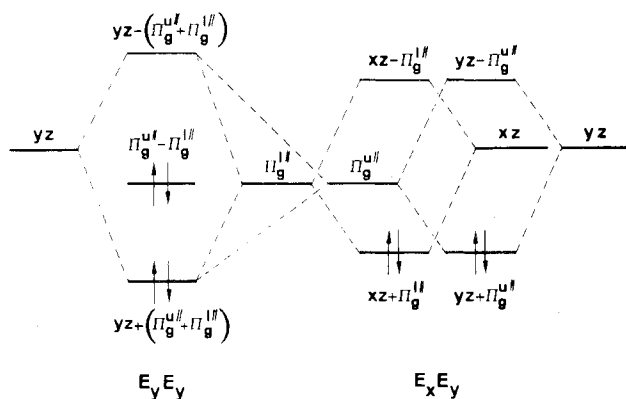


Figure 2.

orbital and the two diatomics. The remaining level (B_{2u}) is a typical nonbonding MO (i.e., no interaction with the metal). The resulting system is then formed by three molecular levels. The qualitative energy diagram arising from the combination of the π_g^{\parallel} with their matching symmetry orbitals of the metal in the two conformations is presented in Figure 2.

In the bis(dioxygen) complex, the molybdenum d levels⁸ will lie close to the ligand π_g^{\parallel} orbitals.⁹ Since d orbitals interact equally with the upper and lower molecules, one obtains a characteristic "allylic" type diagram for E_yE_y and two usual "ethylenic" type diagrams for E_xE_y . In both conformations, two of these levels are to be occupied by four electrons. The total energy is well-known¹⁰ in that case to be lower for two ethylenic systems compared to an allylic one so that the E_xE_y conformation will be the favored one.

The preceding arguments similarly apply to the interactions involving the π_u^{\perp} levels giving an "allylic" system for E_yE_y , vs. two "ethylenic" ones for E_xE_y . Thus the eclipsed conformation found in the dioxygen complexes of titanium and molybdenum porphyrins are well accounted for by simple group-theoretical considerations.

Finally it should also be mentioned that a recent ab initio calculation by Rohmer and Veillard¹¹ found the eclipsed conformation of a dioxygen titanium porphyrin to be more stable than the staggered one. The calculated energy difference is 5 kcal/mol in agreement with the value of 10 kcal/mol evaluated from dynamic NMR measurements.⁴

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References and Notes

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Facile Synthesis of the Lower Valent Halides of Gallium, Ga_2X_4 ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) and Ga_4I_6

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The lower valent halides of gallium are usually prepared by the reduction of gallium(III) halides at temperatures in the region of 180 °C for the chloride and bromide and 212 °C for the iodide.^{1,2} The temperatures are often critical since disproportionation reactions easily occur.

Very pure Ga_2Cl_4 and Ga_2Br_4 may be prepared by the rather tedious process of fractionally freezing the compounds at their melting points.¹ This method cannot be used for Ga_2I_4 since the following disproportionation reaction occurs at its melting point:² $3\text{Ga}_2\text{I}_4 \rightarrow \text{Ga}_4\text{I}_6 + \text{Ga}_2\text{I}_6$.

We have found that the halides Ga_2X_4 ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) and Ga_4I_6 may be easily prepared by reducing the relevant gallium(III) halide with gallium metal at 60 °C in benzene solution.

Experimental Section

Preparation of Ga_2I_4 . Stoichiometric amounts of gallium(III) iodide (4.73 g, 7.17 mmol) and gallium metal (0.25 g, 3.505 mmol) were shaken with benzene in an evacuated glass vessel at 60 °C in an oven. After 1 day all of the metal had been consumed and an insoluble yellow solid of Ga_2I_4 remained. After the mixture was cooled, the benzene was removed by vacuum distillation.

Anal. Calcd for Ga_2I_4 : Ga, 21.5; I, 78.5. Found: Ga, 21.4; I, 78.1.

Raman spectrum: 143 (vs), 214 (w), 235 (w) cm^{-1} .

Preparation of Ga_4I_6 . The method was identical with that described for the diiodide except that an excess of gallium metal was added to the gallium(III) iodide in benzene. For gram quantities of product the reaction was complete in 24 h. A yellow-green solid of Ga_4I_6 was formed.

Anal. Calcd for Ga_4I_6 : Ga, 26.8; I, 73.2. Found: Ga, 26.9; I, 72.8.

Raman spectrum: 292 (s), 186 (w), 124 (vs), 79 (m) cm^{-1} .

Preparation of Ga_2Cl_4 and Ga_2Br_4 . Gallium(III) halide and excess gallium metal were heated with benzene in an evacuated glass vessel at 60 °C for 24 h. After this time two liquid layers had formed. These layers are characteristic of the halides which form benzene complexes.⁴ The benzene was removed by vacuum distillation and white crystalline solids remained.

Anal. Calcd for Ga_2Cl_4 : Ga, 49.6; Cl, 50.4. Found: Ga, 49.4; Cl, 50.1. Calcd for Ga_2Br_4 : Ga, 30.4; Br, 69.6. Found: Ga, 30.1; Br, 70.1. Melting points: Ga_2Cl_4 , 172 °C; Ga_2Br_4 , 166 °C.

Raman spectra: Ga_2Cl_4 377 (m), 347 (vs), 174 (w), 150 (m), 115 (w); Ga_2Br_4 273 (w), 269 (w), 210 (vs), 109 (m).

Drying of Benzene. Since the halides are very susceptible to moisture, "sodium dried" benzene was refluxed for 12 h with lithium hydride and fractionally distilled. The solvent was then tested by the addition of a small amount of gallium "dihalide". Minute traces of

water may be detected by this method since hydrolysis produces a characteristic brown precipitate.

Analysis. Gallium was determined gravimetrically as the 8-hydroxyquinolate. Halogen was determined by argentometric titration. Raman spectra were recorded on a Cary 81L spectrometer and compared with previously recorded spectra.^{2,3}

Discussion

The methods describe the preparation of pure Ga_2X_4 ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) and Ga_4I_6 and are clearly superior to the normal high-temperature methods. Purity is assessed by chemical analysis, melting points for Ga_2Cl_4 and Ga_2Br_4 (Ga_2I_4 and Ga_4I_6 decompose when heated), and Raman spectra which compare very favorably with those obtained from samples prepared by other methods.

The subhalides Ga_4X_6 ($\text{X} = \text{Br}, \text{I}$) are of interest since they are believed to contain metal-metal bonds and may thus be formulated $(\text{Ga}^+)_2\text{Ga}_2\text{X}_6^{2-}$. Evidence for this formulation rather than one based upon a gallium cluster⁶ comes from their Raman spectra which compare very favorably with those of the salts $(\text{R}_4\text{N}^+)_2\text{Ga}_2\text{X}_6^{2-}$. A crystal structure determination has unequivocally shown that the metal-metal bonded ions are present in the chloride salts.⁷ Ga_4Br_6 cannot be prepared by the reduction of gallium(III) bromide with excess gallium metal in benzene solution. A separate experiment has shown that the following decomposition occurs in benzene: $2\text{Ga}_4\text{Br}_6 \rightarrow 3\text{Ga}_2\text{Br}_4 + 2\text{Ga}$.

Registry No. Ga_2I_4 , 17845-89-5; Ga_4I_6 , 33088-29-8; Ga_2Cl_4 , 24597-12-4; Ga_2Br_4 , 18897-61-5; GaI_3 , 13450-91-4; GaCl_3 , 13450-90-3; GaBr_3 , 13450-88-9.

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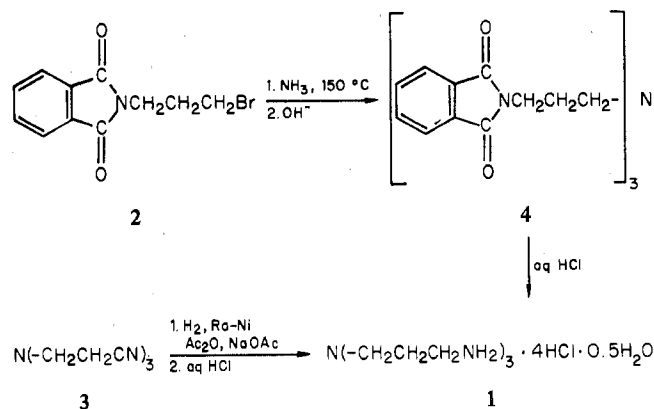
A Convenient Synthesis of $\text{N}(\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_2)_3 \cdot 4\text{HCl} \cdot 0.5\text{H}_2\text{O}$

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In order to synthesize certain polyamine chelating agents, we required as an intermediate 3,3',3''-triaminotripropylamine tetrahydrochloride (**1**). This ligand may be prepared from 1-bromo-3-phthalimidopropane (**2**, Scheme I) in extremely low¹ yield by the procedure of Mann and Pope.² Workers who recently have studied metal complexes of the free base derived from **1** were unable to obtain the ligand by other methods, including the catalytic reduction of tris(β -cyanoethylamine) (**3**). However, others have succeeded in preparing **1** in 44% yield by reducing **3** with Raney nickel (Ra-Ni) and hydrogen (3200 psi) at 120 °C.³ Conducting the reduction in the presence of ammonia presumably suppressed polymerization and/or cyclization products expected from the inter- and intramolecular addition of $\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_2$ fragments with $\text{CH}_2\text{CH}_2\text{CH}=\text{NH}$ fragments.⁴ These side reactions also may be blocked by performing nitrile reductions in acetic anhydride solvent using Ra-Ni and sodium acetate.⁴ The resulting amine functions are trapped as the *N*-acetyl derivatives; hydrolysis

Scheme I



of the reduction products under either basic or acidic conditions may be used to obtain the amines as free bases or salts, respectively. We report here the application of this procedure to the hydrogenation of **3** at low pressure (50 psig). Subsequent acid hydrolysis of the reduction product has afforded **1** in 86% overall yield.

Experimental Section

1. Reduction of 3. The trinitrile (**3**) was prepared in 90% yield from the reaction of acrylonitrile with aqueous ammonia following a published procedure.³ Excess acrylonitrile and water were removed by rotary evaporation (aspirator pressure, ~95 °C). The resulting brown syrup was dried by the addition of 50 mL of absolute ethanol and further rotary evaporation. Instead of purifying **3** by distillation,³ we obtained this crystalline product by stirring a mixture of the brown syrup and absolute alcohol at room temperature. The crude product was collected by filtration. After a single recrystallization from warm ethanol, the product melted at 56–58 °C (lit.³ mp 58–59 °C).

A repetition of the reported rapid and quantitative reduction of adiponitrile to *N,N*-diacetyl-1,6-hexanediamine⁴ was used to calibrate the Parr hydrogenation apparatus and to demonstrate the activity of the Ra-Ni catalyst.^{5a} A water suspension of the catalyst was dried immediately before using by repeated washing (decantation) with absolute ethanol and, finally, with acetic anhydride. About 3 mL of the catalyst (wet with acetic anhydride) was added to a 500-mL Parr bottle along with 26.4 g (0.15 mol) of **3**, 12.0 g (0.15 mol) of sodium acetate, and 200 mL of acetic anhydride. The quantitative amount of hydrogen was absorbed after 6 h when the reaction was performed at 65–75 °C and 50 psig hydrogen pressure. The sodium acetate was removed by filtration, and the filtrate was concentrated to a thick yellow syrup by rotary evaporation (aspirator pressure, 95 °C). We did not attempt to obtain the *N*-acetyl derivative in crystalline form. The ¹H NMR spectrum of the yellow syrup in deuteriochloroform solution was consistent with the reduction product being the monoacetate salt of tris(3-acetamidopropyl)amine. The nitrile infrared absorption at ~2250 cm^{-1} of the starting material could not be detected in the reduction product.

2. Acid Hydrolysis of the Reduction Product. A solution of the yellow syrup in 100 mL of 37% aqueous hydrochloric acid was refluxed for 12 h. During this time the color of the mixture turned dark brown. Rotary evaporation (aspirator pressure, 95 °C) of the reaction mixture yielded a dark brown solid residue. The residue was dried further by the azeotropic rotary evaporation of remaining water with two 50-mL portions of absolute ethanol. The addition of 200 mL of absolute ethanol to the residue followed by extensive stirring and shaking yielded a tan solid and a brown supernatant liquid which was decanted and discarded. The tan solid was triturated again with 100 mL of absolute ethanol, collected by filtration, and dried in a vacuum oven (aspirator pressure, 90 °C). Forty-four grams (86%) of tan solid was obtained which melted with foaming at 220–222 °C (lit.² mp 227–229 °C). Anal. Calcd for $\text{C}_9\text{H}_{25}\text{N}_4\text{Cl}_4\text{O}_{0.5}$ (**1**): C, 31.49; H, 8.45; N, 16.33; Cl, 41.34. Found: C, 31.61; H, 8.66; N, 16.07; Cl, 40.74.

The product was adequately pure for our needs, and further purification was not attempted. The chemical identity of the product was established further by the high-yield preparation of two known derivatives.