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Two Ligand-Bridged Phthalocyanines: Crystal and Molecular Structure of Fluoro(phthalocyaninato)gallium(III), $[Ga(Pc)F]_n$, and (μ-Oxo)bis[(phthalocyaninato)aluminum(III)], $[Al(Pc)]_2O$

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A single-crystal X-ray diffraction analysis has been carried out on $[Ga(Pc)F]_n$ and $[Al(Pc)]_2O$ (Pc = phthalocyaninato dianion, $C_{32}H_{20}N_8^{2-}$) to provide a structural basis for the observed chemical stability and volatility of these compounds and the conductivity of $[Ga(Pc)F]_n$ upon doping. $[Ga(Pc)F]_n$ crystallizes in the triclinic space group $P\bar{1}$ with a = 3.8711 (3) Å, b = 12.601 (1) Å, c = 12.793 (1) Å, α = 90.27 (1)°, β = 96.42 (1)°, γ = 91.28 (1)°, and V = 620.0 Å^3. For Z = 1 and fw = 601.26 the calculated density is 1.61 g/cm^3. Automated diffractometer intensity data (Enraf-Nonius CAD4) were used to solve the structure. Refinement led to R_f = 4.1% and R_{wF} = 5.7% for 2545 unique reflections with 2.8° < 2θ < 150° (Cu Kα radiation). Gallium is octahedrally coordinated by two fluorine atoms and four nitrogens of a virtually planar Pc ring. An inversion center at Ga results in identical trans bond distances (Å): Ga–F(1), 1.936 (1); Ga–N(1), 1.969 (2); Ga–N(2), 1.970 (2). The presence of fluorine in a symmetric bridging position results in a cofacial bridged-stacked structure of eclipsed Pc rings with an interplanar spacing of 3.872 (2) Å. $[Al(Pc)]_2O$ also crystallizes in the triclinic space group $P\bar{1}$ with a = 7.694 (2) Å, b = 12.520 (3) Å, c = 12.705 (3) Å, α = 91.03 (2)°, β = 94.54 (2)°, γ = 90.37 (2)°, and V = 1219.8 Å^3. For Z = 1 and fw = 1095.04, the calculated density is 1.49 g/cm^3. Aluminum is pentacoordinate with four Pc nitrogens forming the base and oxygen the apex of a square pyramid (Å): Al–N(1), 1.994 (5); Al–N(2), 1.978 (5); Al–N(3), 1.968 (5); Al–N(4), 1.973 (5); Al–O, 1.679 (2). The oxygen atom, which is at an inversion center, bridges the two Al(Pc) groups. Thus, the Pc rings are in an eclipsed conformation with an interplanar spacing of 4.27 (2) Å. The dimeric molecules are stacked along the a axis with an intermolecular ring spacing of 3.60 (2) Å.

Introduction

There has recently been considerable interest in group 13 and 14[30] phthalocyanines because of the high conductivity of partially oxidized derivatives,[2–4] interesting cofacial polymeric structures,[3–7] and the thermal and hydrolytic robustness of these materials.[2–9] The cofacially joined metallomacrocyclic polymers $[M(Pc)O]_n$ (M = Si, Ge; Pc = phthalocyanine) may be partially oxidized with a variety of reagents, such as I_2, to give stable, conducting materials.[3] In previous papers, the preparation and conductivity of partially oxidized, isoelectronic, group 13 polymers $[M(Pc)F]_n$ have been described[2,10] and preliminary accounts of the structure of $[Ga(Pc)F]_n$ have appeared.[5,11] The effort below focuses on the complete description of the structure of $[Ga(Pc)F]_n$, and on the structure of $[Al(Pc)]_2O$, a molecule related to $[Ga(Pc)F]_n$ by virtue of a cofacial ring structure.

Experimental Section[12]

General Considerations. $[Ga(Pc)F]_n$[9] and $[Al(Pc)]_2O$[13] were prepared by the methods described by Kenney. Dark purple needlelike crystals of $[Ga(Pc)F]_n$ and $[Al(Pc)]_2O$ were obtained by vacuum sublimation (10^{-3} torr) at approximately 480 °C. Crystals of $[Ga(Pc)F]_n$ and $[Al(Pc)]_2O$ were mounted on glass fibers with the long axis roughly parallel to the φ axis of the goniometer. Crystal data and other parameters for the X-ray diffraction studies may be found in Table I. The experimental method has been described previously.[14] In an examination of ψ scans, appreciable absorptions were not observed for either of the crystals. Extinction corrections were not necessary.

Table I. Experimental Data for the X-ray Diffraction Study of $[Ga(Pc)F]_n$ and $[Al(Pc)]_2O$

	$[Ga(Pc)F]_n$	$[Al(Pc)]_2O$
(A) Crystal Parameters		
temp, °C	23 ± 1	−110 ± 1
cryst dimens, mm	0.02 × 0.15 × 0.40	0.03 × 0.05 × 0.35
cryst syst	triclinic	triclinic
space group	$P\bar{1}$	$P\bar{1}$
a, Å	3.8711 (3)	7.694 (2)
b, Å	12.601 (1)	12.520 (3)
c, Å	12.793 (1)	12.705 (3)
α, deg	90.27 (1)	91.03 (2)
β, deg	96.42 (1)	94.54 (2)
γ, deg	91.28 (1)	90.37 (2)
V, Å^3	620.00	1219.8
Z	1	1
mol wt	601.26	1095.04
calcd density, g/cm^3	1.61	1.49
(B) Measurement of Data		
radiation	Cu Kα (λ = 1.541 84 Å)	
monochrometer	graphite cryst, incident beam	
2θ range, deg	2.8–150	
scan type	coupled ω–θ	
scan rate, deg/min	2–20	
scan range	0.6 + 0.300 tan θ	0.8 + 0.300 tan θ
reflcns collected		
total	2665	5202
unique	2545	5018
stds	3 representative reflcns/41 min; no changes	3 representative reflcns/50 min; no changes
corrections	Lorentz–polarization	

Structure Solution and Refinement. $[Ga(Pc)F]_n$. The structure of $[Ga(Pc)F]_n$ was solved with use of the Patterson heavy-atom method, which revealed the position of the Ga atom at the origin. The remaining atoms were located in succeeding difference Fourier syntheses. Hydrogen atoms were located, and their positions and isotropic thermal parameters were refined. The structure was refined by full-matrix least squares, minimizing the function $\sum w(|F_o| - |F_c|)^2$, as described in detail previously.[14] The final cycle of refinement included 225 variable parameters

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Table II. Positional Parameters and Their Esd's for $[Ga(Pc)F]_n$[a]

	x	*y*	*z*
Ga	0.0000	0.0000	0.0000
F	−0.5000	0.0000	0.0000
N(1)	0.0762 (8)	0.0725 (2)	0.1376 (2)
N(2)	0.0069 (8)	0.1383 (2)	−0.0709 (2)
N(3)	0.0814 (8)	−0.0802 (2)	0.2534 (2)
N(4)	0.1522 (8)	0.2540 (2)	0.0811 (2)
C(1)	0.110 (1)	0.0228 (2)	0.2330 (2)
C(2)	0.199 (1)	0.1026 (2)	0.3155 (2)
C(3)	0.236 (1)	0.0935 (3)	0.4234 (3)
C(4)	0.360 (1)	0.1848 (3)	0.4807 (3)
C(5)	0.387 (1)	0.2821 (3)	0.4312 (3)
C(6)	0.321 (1)	0.2919 (3)	0.3233 (3)
C(7)	0.223 (1)	0.1994 (2)	0.2653 (2)
C(8)	0.143 (1)	0.1793 (2)	0.1539 (2)
C(9)	0.089 (1)	0.2341 (2)	−0.0214 (2)
C(10)	0.111 (1)	0.3153 (2)	−0.1011 (2)
C(11)	0.189 (1)	0.4230 (2)	−0.0927 (3)
C(12)	0.189 (1)	0.4795 (3)	−0.1851 (3)
C(13)	0.109 (1)	0.4309 (3)	−0.2817 (3)
C(14)	0.036 (1)	0.3228 (3)	−0.2911 (3)
C(15)	0.036 (1)	0.2654 (2)	−0.1986 (2)
C(16)	−0.020 (1)	0.1536 (2)	−0.1781 (2)

[a] A listing of positional and thermal parameters and their esd's for all atoms, including hydrogens, is available in Table II-S of the supplementary material.

Table III. Positional Parameters and Their Esd's for $[Al(Pc)]_2O$[a]

	x	*y*	*z*
Al	0.2128 (3)	0.0229 (2)	−0.0120 (2)
O	0.0000 (0)	0.0000 (0)	0.0000 (0)
N(1)	0.3290 (8)	−0.1044 (5)	0.0531 (5)
N(2)	0.2876 (8)	0.1028 (5)	0.1198 (5)
N(3)	0.2126 (8)	0.1616 (5)	−0.0825 (5)
N(4)	0.2547 (8)	−0.0425 (5)	−0.1500 (5)
N(5)	0.3545 (9)	−0.0462 (6)	0.2375 (5)
N(6)	0.2180 (8)	0.2832 (5)	0.0691 (5)
N(7)	0.1734 (9)	0.1029 (5)	−0.2661 (5)
N(8)	0.3207 (8)	−0.2248 (5)	−0.0980 (5)
C(1)	0.346 (1)	−0.1177 (6)	0.1595 (6)
C(2)	0.323 (1)	0.0569 (6)	0.2172 (7)
C(3)	0.319 (1)	0.1371 (7)	0.3010 (6)
C(4)	0.346 (1)	0.1270 (8)	0.4107 (7)
C(5)	0.322 (1)	0.2215 (8)	0.4704 (7)
C(6)	0.279 (1)	0.3196 (8)	0.4213 (7)
C(7)	0.258 (1)	0.3272 (7)	0.3112 (7)
C(8)	0.278 (1)	0.2324 (7)	0.2521 (6)
C(9)	0.260 (1)	0.2095 (6)	0.1397 (6)
C(10)	0.198 (1)	0.2605 (6)	−0.0342 (7)
C(11)	0.152 (1)	0.3407 (7)	−0.1125 (7)
C(12)	0.125 (1)	0.4516 (7)	−0.1016 (7)
C(13)	0.081 (1)	0.5071 (8)	−0.1942 (7)
C(14)	0.067 (1)	0.4549 (7)	−0.2941 (8)
C(15)	0.096 (1)	0.3426 (7)	−0.3036 (7)
C(16)	0.138 (1)	0.2879 (7)	−0.2105 (6)
C(17)	0.178 (1)	0.1767 (7)	−0.1893 (6)
C(18)	0.214 (1)	0.0014 (7)	−0.2461 (6)
C(19)	0.211 (1)	−0.0784 (6)	−0.3299 (6)
C(20)	0.171 (1)	−0.0737 (7)	−0.4380 (7)
C(21)	0.178 (1)	−0.1674 (8)	−0.4987 (7)
C(22)	0.225 (1)	−0.2657 (7)	−0.4486 (7)
C(23)	0.264 (1)	−0.2720 (7)	−0.3383 (7)
C(24)	0.254 (1)	−0.1749 (7)	−0.2810 (7)
C(25)	0.281 (1)	−0.1507 (6)	−0.1684 (6)
C(26)	0.343 (1)	−0.2000 (7)	0.0038 (7)
C(27)	0.382 (1)	−0.2814 (7)	0.0827 (7)
C(28)	0.406 (1)	−0.3921 (7)	0.0729 (7)
C(29)	0.433 (1)	−0.4498 (7)	0.1659 (7)
C(30)	0.438 (1)	−0.3958 (7)	0.2666 (7)
C(31)	0.414 (1)	−0.2857 (7)	0.2756 (8)
C(32)	0.385 (1)	−0.2299 (6)	0.1812 (6)

[a] A listing of positional and thermal parameters and their esd's for all atoms is available in Table III-S of the supplementary material.

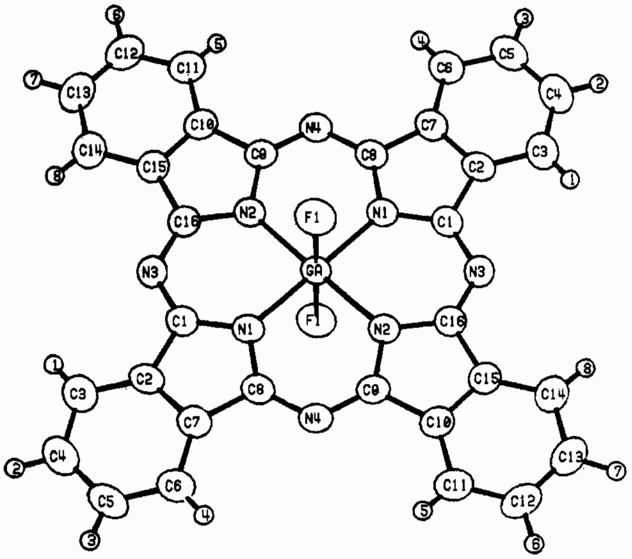

Figure 1. Portion of the $[Ga(Pc)F]_n$ structure with atoms labeled.

and converged, with the largest parameter shift of 0.04 esd, with unweighted and weighted agreement factors of $R_1 = 0.041$ and $R_2 = 0.057$, respectively. The standard deviation of an observation of unit weight was 1.87. The final difference Fourier map showed no significant residual electron density. The highest peak in the final difference Fourier had a height of 0.12 e/Å^3 with an estimated error based on ΔF of 0.04. Final positional parameters are collected in Table II. Supplementary Table I-S contains positional and thermal parameters and their estimated standard deviations (esd's). General temperature factor exprressions may be found in Supplementary Tables II-S (*U*'s) and III-S (*B*'s). Values of observed and calculated structure factor amplitudes are given in Supplementary Table VIII-S.

$[Al(Pc)]_2O$. The structure of $[Al(Pc)]_2O$ was solved by direct methods. With use of 500 reflections with minimum *E* of 1.70 and 2000 relationships, 128 phase sets were produced. A total of 40 atoms were located from an *E* map prepared from the phase set with an absolute figure of merit of 0.93 and residual of 0.36. The remaining atoms were located in succeeding difference Fourier syntheses. Hydrogen atoms were not included in the calculations. The structure was refined as described previously[14] and above by full-matrix least squares. Only the 2385 reflections having intensities greater than 3.0 times their standard deviation were used in the refinements. The final cycle of refinement included 376 variable parameters and converged with the largest parameter shift of 0.01 esd, with $R_1 = 0.090$ and $R_2 = 0.118$. The standard deviation of an observation of unit weight was 2.33. The highest peak in the final difference Fourier had a height of 0.89 e/Å^3 with an estimated error based on ΔF of 0.17. The highest peaks were in positions expected for hydrogen atoms. Final positional parameters are collected in Table III. Supplementary Table IX-S contains positional and thermal parameters and their esd's. Supplementary Table X-S lists general temperature factor expressions (*B*'s). Observed and calculated structure factor amplitudes are given in Supplementary Table XV-S.

Results and Discussion

$[Ga(Pc)F]_n$. The structure of fluoro(phthalocyaninato)gallium(III) is shown in Figure 1, which also illustrates the numbering scheme. Supplementary Figure 1-S shows a stereoview of the unit cell and indicates the molecular stacking. Important intramolecular distances and angles with associated esd's are listed in Tables IV and V, respectively, while a complete set of data is available as supplementary material (Supplementary Tables IV-S and V-S). Distances from the least-squares plane formed by the coordinated nitrogen atoms N(1)–N(4) are given in Table VI. Distances from additional least-squares planes are provided in Supplementary Table VI-S.

In $[Ga(Pc)F]_n$, Ga is octahedrally coordinated by four nitrogen and two fluorine atoms. The gallium atom is at an inversion center, and thus the trans Ga–F and Ga–N bonds have identical bond distances. Another consequence of the inversion center is the location of the fluorine atoms in a symmetric bridging position (Ga–F = 1.936 (1) Å). Surprisingly, this Ga–F distance is only slightly longer than single bond distances seen in $LiMnGaF_6$[15]

Table IV. Interatomic Distances (Å) with Esd's for (A) $[Ga(Pc)F]_n$ and (B) $[Al(Pc)]_2O$[a]

	A. $[Ga(Pc)F]_n$		
Ga-F	1.936 (1)	N(2)-C(9)	1.375 (3)
Ga-N(1)	1.969 (2)	N(2)-C(16)	1.379 (3)
Ga-N(2)	1.970 (2)	N(3)-C(1)	1.330 (3)
N(1)-C(1)	1.369 (3)	N(3)-C(16)	1.329 (3)
N(1)-C(8)	1.375 (3)	N(4)-C(8)	1.330 (3)
		N(4)-C(9)	1.328 (3)
	B. $[Al(Pc)]_2O$		
Al-O	1.679 (2)	N(4)-C(18)	1.362 (7)
Al-N(1)	1.994 (5)	N(4)-C(25)	1.389 (7)
Al-N(2)	1.978 (5)	N(5)-C(1)	1.324 (7)
Al-N(3)	1.968 (5)	N(5)-C(2)	1.340 (7)
Al-N(4)	1.973 (5)	N(6)-C(9)	1.323 (7)
N(1)-C(1)	1.364 (7)	N(6)-C(10)	1.335 (7)
N(1)-C(26)	1.350 (7)	N(7)-C(17)	1.330 (7)
N(2)-C(2)	1.382 (7)	N(7)-C(18)	1.335 (7)
N(2)-C(9)	1.376 (7)	N(8)-C(25)	1.321 (7)
N(3)-C(10)	1.382 (7)	N(8)-C(26)	1.322 (7)
N(3)-C(17)	1.379 (7)		

[a] Distances to and within the peripheral phenyl groups may be found in the supplementary material.

Table V. Interatomic Angles (deg) for (A) $[Ga(Pc)F]_n$ and (B) $[Al(Pc)]_2O$

	A. $[Ga(Pc)F]_n$[a]		
F(1)-Ga-F(1)	180.00	C(1)-N(1)-C(8)	108.6 (2)
F(1)-Ga-N(1)	92.25 (7)	Ga-N(2)-C(9)	125.1 (2)
F(1)-Ga-N(1)	87.75 (7)	Ga-N(2)-C(16)	125.7 (2)
F(1)-Ga-N(2)	92.60 (7)	C(9)-N(2)-C(16)	108.6 (2)
F(1)-Ga-N(2)	87.40 (7)	C(1)-N(3)-C(16)	122.8 (2)
F(1)-Ga-N(1)	87.75 (7)	C(8)-N(4)-C(9)	123.1 (2)
F(1)-Ga-N(1)	92.25 (7)	N(1)-C(1)-N(3)	128.7 (2)
F(1)-Ga-N(2)	87.40 (7)	N(1)-C(1)-C(2)	108.7 (2)
F(1)-Ga-N(2)	92.60 (7)	N(3)-C(1)-C(2)	122.7 (2)
N(1)-Ga-N(1)	180.00	N(1)-C(8)-N(4)	127.3 (2)
N(1)-Ga-N(2)	89.93 (8)	N(1)-C(8)-C(7)	109.1 (2)
N(1)-Ga-N(2)	90.07 (8)	N(4)-C(8)-C(7)	123.6 (2)
N(1)-Ga-N(2)	90.07 (8)	N(2)-C(9)-N(4)	128.3 (2)
N(1)-Ga-N(2)	89.93 (8)	N(2)-C(9)-N(10)	108.6 (2)
N(2)-Ga-N(2)	180.00	N(4)-C(9)-C(10)	123.1 (2)
Ga-F(1)-Ga	180.00	N(2)-C(16)-N(3)	127.4 (2)
Ga-N(1)-C(1)	125.1 (2)	N(2)-C(16)-C(15)	108.9 (2)
Ga-N(1)-C(8)	125.9 (2)	N(3)-C(16)-C(15)	123.7 (2)
	B. $[Al(Pc)]_2O$[b]		
Al-O-Al	180.00	Al-N(3)-C(10)	125.9 (4)
O(1)-Al-N(1)	103.7 (2)	Al-N(3)-C(17)	125.5 (4)
O(1)-Al-N(2)	103.0 (2)	C(10)-N(3)-C(17)	106.3 (5)
O(1)-Al-N(3)	102.9 (2)	Al-N(4)-C(18)	125.9 (4)
O(1)-Al-N(4)	104.1 (2)	Al-N(4)-C(25)	125.1 (4)
N(1)-Al-N(2)	87.4 (2)	C(18)-N(4)-C(25)	106.6 (5)
N(1)-Al-N(3)	153.4 (2)	C(1)-N(5)-C(2)	120.6 (5)
N(1)-Al-N(4)	86.8 (2)	C(17)-N(7)-C(18)	121.4 (5)
N(2)-Al-N(3)	86.6 (2)	C(25)-N(8)-C(26)	120.8 (5)
N(2)-Al-N(4)	152.9 (2)	N(1)-C(1)-N(5)	129.7 (5)
N(3)-Al-N(4)	86.9 (2)	N(2)-C(9)-N(6)	126.6 (5)
Al-N(1)-C(1)	123.5 (4)	N(3)-C(10)-N(6)	127.0 (5)
Al-N(1)-C(26)	124.7 (4)	N(3)-C(17)-N(7)	127.3 (5)
C(1)-N(1)-C(26)	109.0 (5)	N(4)-C(18)-N(7)	127.4 (6)
Al-N(2)-C(2)	124.7 (4)	N(4)-C(25)-N(8)	127.8 (5)
Al-N(2)-C(9)	126.2 (4)	N(1)-C(26)-N(8)	129.4 (5)
C(2)-N(2)-C(9)	106.1 (5)	N(2)-C(2)-N(5)	127.6 (6)

[a] Angles within the phenyl groups involving C-H bonds may be found in the supplementary material. [b] Angles to and within the phenyl groups may be found in the supplementary material.

(1.883–1.905 (3) Å) and GaF_3[16] (1.89 Å).

An unusual feature of the $[Ga(Pc)F]_n$ structure is the long interplanar ring spacing (3.872 (2) Å), which is a result of the covalent/coordinate-covalent F-bridged structure. In isoelectronic $[Ge(Pc)O]_n$, where two covalent bonds are formed through O bridging, a shorter interplanar spacing is observed (3.59 Å).[3] As a consequence of the long interplanar spacing in $[Ga(Pc)F]_n$, the Pc rings are in an eclipsed conformation as discussed further below with reference to Table VII.

The Ga–N distances of 1.969 (2) and 1.970 (2) Å are slightly shorter than those observed for Ga(Pc)Cl[14] (1.979–1.988 (4) Å). This is a consequence of the coplanarity of Ga with the Pc ring in $[Ga(Pc)F]_n$, whereas Ga is 0.439 (1) Å above the ring in Ga(Pc)Cl. The Ga–N distances in $[Ga(Pc)F]_n$ are substantially shorter than a number of gallium complexes containing nonmacrocylic ligands (2.1–2.2 Å).[17-19]

Table VI. Distances from the Least-Squares Plane Formed by (A) N(1)–N(2)′ for $[Ga(Pc)F]_n$ and (B) N(1)–N(4) for $[Al(Pc)]_2O$[a,b]

	x	*y*	*z*	dist, Å
		A. $[Ga(Pc)F]_n$[c]		
N(1)	0.0775	0.9005	1.7498	0.000
N(2)	0.0893	1.7488	−0.9015	0.000
N(1)′	−0.0775	−0.9005	−1.7498	0.000
N(2)′	−0.0893	−1.7488	0.9015	0.000
Ga	0.0000	0.0000	0.0000	0.000
F(1)	−1.9356	0.0000	0.0000	−1.982
C(1)	0.0866	0.2656	0.9626	0.029
C(8)	0.2817	2.2442	1.9560	0.123
C(9)	0.3083	2.9513	−0.2721	0.140
C(16)	0.1333	1.9511	−2.2647	0.052
		B. $[Al(Pc)]_2O$		
N(1)	2.4865	−1.3200	0.6723	−0.003 (6)
N(2)	2.0840	1.2589	1.5171	0.003 (6)
N(3)	1.7058	2.0421	−1.0447	−0.004 (6)
N(4)	2.1141	−0.4973	−1.8997	0.003 (6)
Al	1.6472	0.2899	−0.1513	−0.459 (2)
O(1)	0.0000	0.0000	0.0000	−2.138
N(5)	2.4919	−0.6341	3.0069	−0.072 (7)
N(6)	1.5848	3.5296	0.8744	−0.013 (7)
N(7)	1.5937	1.3506	−3.3690	−0.041 (7)
N(8)	2.5840	−2.7916	−1.2412	−0.014 (7)
C(1)	2.5880	−1.5105	2.0192	−0.055 (8)
C(2)	2.2633	0.6614	2.7508	−0.036 (8)
C(9)	1.8438	2.5903	1.7695	−0.009 (8)
C(10)	1.5341	3.2692	−0.4336	0.001 (8)
C(17)	1.5419	2.2572	−2.3970	−0.009 (8)
C(18)	1.8960	0.0751	−3.1159	−0.001 (8)
C(25)	2.3401	−1.8477	−2.1320	−0.003 (8)
C(26)	2.6520	−2.5049	0.0478	−0.005 (8)

[a] A complete listing of least-squares planes, which includes phenyl carbon atoms, may be found in the supplementary material. [b] The equation of the plane is of the usual form $A^*x + B^*y + C^*z - D = 0$. The values of *A*, *B*, *C*, and *D* are respectively as follows: for $[Ga(Pc)F]_n$ 0.9982, −0.0583, −0.0142, and 0.0000; for $[Al(Pc)]_2O$ 0.9793, 0.1836, −0.0857, and 2.1384.

Table VII. Interplanar Spacings and Staggering Angles for Cofacially Stacked M(Pc)-Containing Structures

compd	ref	interplanar spacing, Å	staggering angle, deg
Ni(Pc)I	20	3.244 (2)	39.5
$[Gi(Pc)O]_n$	3, 9	3.33 (2)	39 (3)
$[Mn(Pc)(py)]_2O$[a]	21	3.42 (4)	49
$([Ge(Pc)O]I_{1.07})_n$	4	3.48 (2)	40 (4)
$[Ge(Pc)O]_n$	3	3.53 (2)	0
$[Ga(Pc)F]_n$	this work	3.872 (2)	0
$[Al(Pc)]_2O$	this work	4.276	0

[a] py = pyridine.

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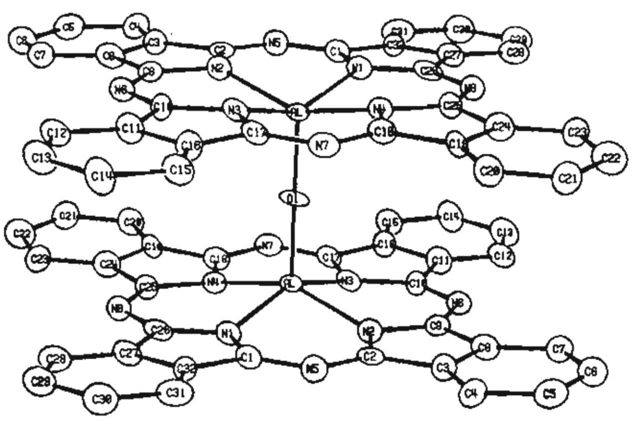

Figure 2. The $[Al(Pc)]_2O$ molecule with atoms labeled.

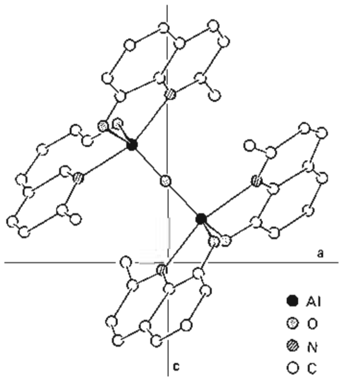

Figure 3. Structure of (μ-oxo)bis(2-methyl-8-quinolinolato)aluminum(III).[22]

The facility with which the Pc ring accommodates Ga within the ring in $[Ga(Pc)F]_n$ or above the ring in Ga(Pc)Cl[14] is worth noting. The *trans*-N(1)–Ga–N(1) distance in $[Ga(Pc)F]_n$ is 3.94 Å while the comparable distance in Ga(Pc)Cl is 3.87 Å.

The bond angles for the trans-coordinated atoms are exactly 180° as required by the crystallographic inversion center. However, there is a slight cant (e.g., F(1)–Ga–N(1) = 87.75 (7)°) of the F–Ga–F axis with respect to the N(1)–N(4) plane.

Finally, it should be noted that a fluoro(macrocycle)metal(III) composition does not always lead to a bridged–stacked structure. Thus, fluoro(*meso*-tetraphenylporphinato)iron(III) forms a molecular crystal, with the out-of-plane (0.47 Å) iron having square-pyramidal coordination.[22]

$[Al(Pc)]_2O$. The structure of (μ-oxo)bis[(phthalocyaninato)aluminum(III)] is shown in Figure 2, together with the numbering scheme. A stereoview of the unit cell is shown in Supplementary Figure 2-S and indicates the molecular stacking. Important intramolecular distances and angles with associated esd's are listed in Tables IV and V, respectively, while a complete set of data is available in Supplementary Tables XI-S and XII-S. Distances from the least-squares plane formed by the coordinated nitrogen atoms N(1)–N(4) are given in Table VI. Distances from additional least-squares planes are provided in Supplementary Table XIII-S.

In $[Al(Pc)]_2O$, Al is pentacoordinate, with the Pc nitrogens N(1)–N(4) forming the base and oxygen the apex of a square pyramid (Figure 3). Two Al(Pc) units are joined at the commonly shared apex, resulting in a symmetric, dimeric structure. The aluminum atom is 0.459 (2) Å above the least-squares plane formed by N(1)–N(4).

The oxygen atom is at an inversion center, and the Pc rings are therefore eclipsed and are in parallel planes, with an interplanar spacing of 4.27 (2) Å. The eclipsed conformation for $[Al(Pc)]_2O$ may be compared with the conformations found for a number of related M(Pc)-containing systems shown in Table VII. These data indicate that the sterically less crowded staggered conformation is preferred when interplanar spacing is less than 3.5 Å, while the eclipsed conformation occurs at larger spacings. An interesting crossover from eclipsed to staggered conformation occurs for $[Ge(Pc)O]_n$ on partial oxidation with iodine to $([Ge(Pc)O]I_{1.07})_n$, as shown by Marks.[3,4]

Although Al is out of plane, the Al–N distances of 1.968–1.994 Å are less than those observed for structures not containing macrocyclic rings (2.1–2.2 Å).[23,24]

Al–O bonds in Al–O–M (M = metal) groups generally contain tetrahedrally coordinated aluminum and display Al–O distances of 1.8 Å. An example of a long bond (Al–O, = 1.842 (9) Å) is found in $[(CH_3)_3AlO(O)Al(CH_3)_3]^-)$,[25] while a short distance (1.751 (3) Å) is found in $W(\eta^2\text{-}HC{\equiv}COAlCl_3)(CO)[P(CH_3)_3]Cl$.[26] The Al–O distance of 1.679 (2) Å in $[Al(Pc)]_2O$ is considerably shorter than these values but compares favorably with the 1.68 (1.3) Å distance found for (μ-oxo)bis(2-methyl-8-quinolinolato)aluminum(III) (Figure 3), which also contains a linear Al–O–Al group, but with trigonal-bipyramidal geometry about aluminum.[23] The short Al–O distances in both linear Al–O–Al groups indicate these bonds have significant double-bond character achieved through pπ–dπ bonding.

As Supplementary Figure 2-S shows, the $[Al(Pc)]_2O$ molecules form stacks down the *a* axis, with an intermolecular ring–ring stacking distance of 3.60 (2) Å. It is interesting that the intermolecular ring separation is 0.67 Å shorter than the intramolecular separation. This observation suggests that an investigation of the partial oxidation of $[Al(Pc)]_2O$ might be interesting for the examination of the consequences of a "built-in" Pierls distortion[27,28] in the molecular stacking direction.

Conclusion

In view of the long interplanar spacing of 3.872 Å in $[Ga(Pc)F]_n$ it is suprising that highly conducting partially oxidized materials are easily derivable, as previous results on partially oxidized $[M(Pc)OI_x]_n$ (M = Si, Ge, Sn)[3,4] make it likely that the bridged–stacked structure found for $[Ga(Pc)F]_n$ persists in the doped materials. Only a modest contraction (~0.05 Å) of interplanar ring spacing is expected on partial oxidation.[4]

ESR spectroscopy and other lines of evidence indicate that conduction in doped phthalocyanines occurs through a conduction band formed by overlap of pπ orbitals on the Pc ring.[2–4] Thus, the persistence of spacings significantly longer than van der Waals distance for separation of aromatic rings (3.4 Å)[29] would be expected to decrease pπ orbital overlap and increase the activation energy for electron transport. However, an examination of interstack distances for $[Ga(Pc)F]_n$ reveals a number of intermolecular C–C contacts at 3.5 Å, e.g., C(3)–C(3)′ (at −1,1,0,1) = 3.49 (2) Å and C(11)–C(11)′ (at −1,0,1,0) = 3.52 (2) Å. A conduction band could therefore result from interstack pπ interactions if such contacts persisted in the partially oxidized materials (e.g., through layering). Thus, interstack conduction band formation may be important as a mechanism for solid-state charge transport in bridged–stacked Pc materials, such as $[Ga(Pc)F]_n$ derivatives, which have long intrastack distances. This argument finds support in the observation that $[Ga(Pc)FI_{1.18}]_n$[2] and $[Ge(Pc)OI_{1.08}]_n$[4] have comparable conductivities (0.1 S/cm^{-1})

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[30] The group notation is being changed in accord with recent actions by IUPAC and ACS nomenclature committees. A and B notation is being eliminated because of wide confusion. Group I becomes groups 1 and 11, group II becomes groups 2 and 12, group III becomes groups 3 and 13, etc.

and activation energies (0.03 eV), although the interplanar spacing for the Ge material is ~0.3 Å shorter than that of the Ga analogue.

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Supplementary Material Available: Stereoscopic views of the $[Ga(Pc)F]_n$ and $[Al(Pc)]_2O$ unit cells (Figures 1-S and 2-S, respectively) and positional and thermal parameters and esd's (Tables I-S (Ga) and IX-S (Al)), general temperature factor expressions (Tables II-S and III-S (Ga) and X-S (Al)), bond distances and angles (Tables IV-S and V-S (Ga) and XI-S and XII-S (Al)), least-squares planes (Tables VI-S (Ga) and XIII-S (Al)), intermolecular contacts (Tables VII-S (Ga) and XIV-S (Al)), and observed and calculated structure factor amplitudes (Tables VIII-S (Ga) and XV-S (Al)) (55 pages). Ordering information is given on any current masthead page.

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Role of the H_3O_2 Bridging Ligand in Coordination Chemistry. 1. Structure of Hydroxoaquametal Ions

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The structures of two classical, so-called hydroxo aqua complex ions of chromium(III) and cobalt(III) were investigated by single-crystal X-ray diffraction. These structures were shown not to be mononuclear hydroxo aqua ions, with distinct OH and H_2O ligands, but binuclear or polynuclear ions with symmetrical hydrogen oxide bridges (H_3O_2) between the metal atoms. Compound **1**, *cis*-$[Cr(bpy)_2(H_3O_2)]_2I_4{\cdot}2H_2O$, forms orthorhombic crystals, space group *Pbcn*, with $a = 15.511$ (2) Å, $b = 15.115$ (2) Å, $c = 20.955$ (3) Å, $V = 4913$ (1) Å^3, and $Z = 4$. Compound **2**, *trans*-$[Co(en)_2(H_3O_2)](ClO_4)_2$, forms monoclinic crystals, space group $P2_1/c$, with $a = 5.724$ (1) Å, $b = 8.146$ (1) Å, $c = 14.923$ (2) Å, $\beta = 99.17$ (2)°, $V = 687$ (1) Å^3, and $Z = 2$. The two structures were refined by full-matrix least-squares methods to residuals of $R = 0.037$, $R_w = 0.042$ and $R = 0.026$, $R_w = 0.039$, respectively. In structure **1** there are two H_3O_2 units that are symmetry related with an O···O distance of 2.446 (5) Å. In structure **2** the cobalt atom and the central hydrogen atom of the H_3O_2 group reside on crystallographic inversion centers, thus forming infinite chains of ···Co–H_3O_2–Co··· with an O···O distance of 2.441 (2) Å. It is concluded that hydroxo aqua ions do not exist in the crystalline state as such: the so-called cis hydroxo aqua ions are dimers bridged by two H_3O_2 bridges and the so-called trans hydroxo aqua ions are polynuclear chains of metal atoms bridged by single H_3O_2 ligands. The mechanism of olation reactions, in the solid state and in aqueous solutions, is formulated as an elimination of water molecules from H_3O_2 bridges, accompanied by formation of OH bridges between the metal ions.

Introduction

Coordinated hydrogen oxide, $H_3O_2^-$, was first reported and characterized as a bridging ligand between trinuclear, triangular cluster ions of molybdenum and tungsten.[1] In these clusters, generally formulated as $[M_3O_2(O_2CR)_6(H_2O)_3]^{2+}$, each metal atom is coordinated to one water ligand that may hydrolyze to a hydroxo ligand to give $[M_3O_2(O_2CR)_6(H_2O)_2(OH)]^+$. The H_3O_2 ligand is formed by means of a short and symmetrical hydrogen bond between a water ligand of one metal atom and a hydroxo ligand of another metal atom. The distance between the two oxygen atoms in the H_3O_2 unit varies between 2.44 and 2.52 Å in the six structures of cluster salts determined by X-ray crystallography.[1] Two classes of H_3O_2-bridged clusters were discovered: (a) "diclusters" in which two clusters are bridged by a single hydrogen oxide bridge, as in $\{[W_3O_2(O_2CC_2H_5)_6(H_2O)_2]_2(H_3O_2)\}(NCS)_3{\cdot}H_2O$; (b) "polyclusters" in which two of the three metal atoms are linked with the atoms of neighboring clusters by hydrogen oxide bridges, thus forming an infinite cluster chain as in $[W_3O_2(O_2CC_2H_5)_6(H_2O)(H_3O_2)]_n(NCS)_n$. The dicluster and polycluster salts are crystallized by varying the pH of the mother liquor. Formation of the dicluster is favored at a 1:1 ratio of the triaqua cluster and the hydroxo–diaqua cluster, i.e. at pH = pK_1. The polycluster is precipitated at a higher pH in which the hydroxo–diaqua cluster is the predominant monocluster species.[1c]

The starting point of the present investigation was the realization that metal atoms in trinuclear clusters do not have any unique property that makes them more susceptible to hydrogen oxide bridging than ordinary, mononuclear metal ions. This conclusion led to a working hypothesis that hydrogen oxide bridging may be a fundamental, hitherto unrecognized, property of many, if not all, metal ions having H_2O and OH^- ligands.

The strategy employed in the search for evidence for this hypothesis was to grow single crystals of classical hydroxo aqua complexes of chromium(III) and cobalt(III) and to determine their structure by X-ray crystallography. The reason for the choice of Cr(III) and Co(III) was the following. Formation of hydrogen oxide bridged species (reaction 1) was expected to be intimately linked with the "olation" reaction (2) in which more stable

$$[L_5M(OH)]^{(n-1)+} + [(H_2O)ML_5]^{n+} \rightleftarrows [L_5M(H_3O_2)ML_5]^{(2n-1)+} \quad (1)$$

$$[L_5M(H_3O_2)ML_5]^{(2n-1)+} \rightarrow [L_5M(OH)ML_5]^{(2n-1)+} + H_2O \quad (2)$$

μ-hydroxo-bridged species were formed. The hydrogen oxide bridged product of reaction 1 was expected to have a transient existence and only a very low equilibrium concentration, *unless* reaction 2 was very slow. Reaction 1, the hydrogen bond formation, is very fast, probably diffusion controlled. Reaction 2, which involves the breaking of a metal-to-oxygen bond, is slow in trinuclear clusters and any other *inert* complexes. Therefore, the most abundant and common inert complexes, namely those of chromium(III) and low-spin cobalt(III), were investigated first.

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