The complex prepared from copper carbonate follows more closely the behavior of other first-row metal complexes in that, on heating, the proportion of nitrogen-bound component is increased at the expense of the oxygen isomer.

(b) Other Metal Sulfamidates. The only bands observed in the N_{1s} ESCA spectra of the remaining metal sulfamidate complexes (Table II) have values of $\Delta(N_{1s}-S_{2p})$ (231.1 ± 0.2 eV) representitive of sulfamidate ligands in which nitrogen coordination does not occur.

(c) Complexes of Metal Sulfamidates. Studies of the mode of sulfamidate coordination in complexes containing other ligands such as ammine, ethylenediamine, and pyridine further demonstrate the usefulness of ESCA as a technique for quantitative inorganic analysis (Table III). Infrared studies of the complexes with ethylenediamine ligands were complicated because of the overlapping of bands in the N–H regions.[6] However, the ESCA spectra clearly show a single N_{1s} peak with $\Delta(N_{1s}-S_{2p}) = 231.2 \pm 0.2$ eV. Nitrogen in a sulfamidato ligand coordinated to the metal through nitrogen should have a binding energy some 2 eV higher, and this should be evident as a shoulder on the high binding energy side of the N_{1s} band. Simulated N_{1s} spectra consisting of two components separated by 2 eV and having relative intensities of 6 (tris(ethylenediamine)) to 2 (sulfamidato) show that such a shoulder would be readily distinguishable. It can be concluded that the sulfamidato ligand is not coordinated via nitrogen in these complexes. However, it is not possible to distinguish between oxygen coordination (as presumably in $[Ni(en)_2(NH_2SO_3)_2]$) and ionic sulfamidate (as in $[Ni(en)_3](NH_2SO_3)_2$).

The ESCA spectrum of $[Co(NH_3)_5(NH_2SO_3)]^{2+}$ shows a single N_{1s} component with $\Delta(N_{1s}-S_{2p}) = 231.1$ eV, so coordination of the sulfamidate through nitrogen does not occur, although this was suggested as the most likely isomeric form in aqueous solutions.[4] When the doubly deprotonated ligand $(NHSO_3)^{2-}$ is used, coordination through the nitrogen predominates. In this case the nitrogen is a strong Lewis base and is therefore a much more attractive site for coordination than the oxygen.

The ESCA data for the complexes containing pyridine indicate that the sulfamidate ligand is not coordinated through nitrogen. This agrees with earlier conclusions on the mode of coordination for the nickel and cobalt complexes, but not for the copper complex.[6]

Contribution from the Chemistry Departments, University of Florence, 50132 Florence, Italy, and University of Siena, Siena, Italy

Dicopper(II) Complex of the Large Polyazacycloalkane 1,4,7,10,13,16,19,22-Octaazacyclotetracosane (bistrien). Synthesis, Crystal Structure, Electrochemistry, and Thermodynamics of Formation

ANTONIO BIANCHI,[1a] STEFANO MANGANI,[1b] MAURO MICHELONI,[1a] VALERIO NANINI,[1a] PIERLUIGI ORIOLI,[1a] PIERO PAOLETTI,*[1a] and BARBARA SEGHI[1a]

Received May 1, 1984

The large macrocycle 1,4,7,10,13,16,19,22-octaazacyclotetracosane (bistrien) was synthesized. The eight basicity constants and the stability constants of the dinuclear complexes $[Cu_2(bistrien)]^{4+}$, $[Cu_2(bistrien)H_2]^{6+}$, and $[Cu_2(bistrien)OH]^{3+}$ were determined by potentiometry at 25 °C in 0.5 mol dm^{-3} $NaClO_4$. The formation enthalpy of $[Cu_2(bistrien)]^{4+}$ was determined by batch microcalorimetry. The most important species, $[Cu_2(bistrien)]^{4+}$, is extremely stable ($\log k = 36.63$) and exothermic ($-\Delta H^\circ = 39.0$ kcal mol^{-1}), indicating that all nitrogen atoms are involved in the coordination to the metal ions. The stability of the hydroxo species $[Cu_2(bistrien)OH]^{3+}$ is high, and its magnetic susceptibility in solution shows metal–metal interaction. Crystals of the compound $[Cu_2(bistrien)Cl_2](ClO_4)_2$ are monoclinic, space group $P2_1/m$, with $a = 11.811$ (3) Å, $b = 11.352$ (3) Å, $c = 11.385$ (3) Å, $\beta = 99.11$ (4)°, and $Z = 2$. Refinement of the atomic parameters by least squares gave a final R factor of 0.080 ($R_w = 0.070$) for 1340 unique reflections with $F_o > 2\sigma(F_o)$. The structure consists of centrosymmetric binuclear Cu_2(bistrien) units held together by chlorine bridges forming pairs of polymeric ···Cu–Cl–Cu···Cl···Cu zigzag chains parallel to the b axis. The copper atoms are coordinated by four nitrogen atoms of the macrocyclic ligand (average Cu–N = 2.04 (1) Å) and one chloride ion (Cu–Cl = 2.48 (2) Å), forming a distorted square pyramid. One further chloride ion at 3.31 (2) Å completes a distorted elongated octahedron. The electrochemical behavior of the dinuclear complex $[Cu_2(bistrien)]^{4+}$ was investigated in aqueous solution by cyclic voltammetry. The complex undergoes a two-electron reversible reduction into the dinuclear Cu(I) species, by two independent monoelectronic steps. The reduced species is unstable with respect to the demetalation and reduction to metal.

Introduction

The coordination chemistry of the macrocyclic metal complexes has widely grown in recent years.[2] Among polyazamacrocycles the tetraazacycloalkanes are by far the most studied. Many papers have been published dealing with tetraaza macrocycles.[3-5] Much less is instead known about the thermodynamics protonation and metal complex formation of large polyazacycloalkanes (more than six nitrogens as donor atoms), for which only few publications have appeared in literature until now.[6,7] The possibility for these

---

[1] (a) University of Florence. (b) University of Siena.

[2] Izatt, R. M.; Christenses, J. J. "Synthetic Multidentate Macrocyclic Compounds"; Academic Press: New York, 1978. Melson, G. A. "Coordination Chemistry of Macrocyclic Compounds"; Plenum Press: New York, 1979. Hiraoka, M. "Crown Compounds. Their Characteristic and Applications"; Elsevier: Amsterdam, 1982.

[3] Busch, D. H. *Helv. Chim. Acta* **1967**, 174. Curtis, N. F. *Coord. Chem. Rev.* **1968**, *3*, 3. Poon, C. K. *Ibid.* **1973**, *10*, 1. Lindoy, L. F. *Chem. Soc. Rev.* **1975**, *4*, 421.

[4] Cabbiness, D. H.; Margerum, D. W. *J. Am. Chem. Soc.* **1969, 91**, 6540. Martin, L. Y.; Dehayes, L. J.; Zompa, L. J.; Bush, D. H. *Ibid.* **1974, 96**, 4046. Kodama, M.; Kimura, E. *J. Chem. Soc., Dalton Trans.* **1976**, 116. Kodama, M.; Kimura, E. *Ibid.* **1976**, 2335. Steinmann, W.; Kaden, T. A. *Helv. Chim. Acta* **1975**, *58*, 1358.

[5] Fabbrizzi, L.; Paoletti, P.; Clay, R. M. *Inorg. Chem.* **1978**, *17*, 1042. Anichini, A.; Fabbrizzi, L.; Paoletti, P.; Clay, R. M. *J. Chem. Soc., Dalton Trans.* **1978**, 577. Clay, R. M.; Micheloni, M.; Paoletti, P.; Steele, W. V. *J. Am. Chem. Soc.* **1979**, *101*, 4119. Graddon, D. P.; Micheloni, M.; Paoletti, P. *J. Chem. Soc., Dalton Trans.* **1981**, 336. Micheloni, M.; Paoletti, P.; Sabatini, A. *Ibid.* **1983**, 1189.

0020-1669/85/1324-1182$01.50/0

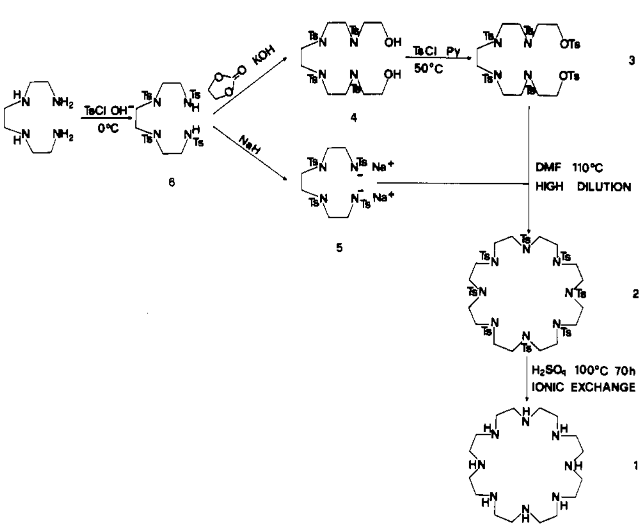

Figure 1. Reaction sequence for the synthesis of the macrocycle bistrien (1).

macrocycles to bind more than one metal ion in the macrocyclic framework and the recent development of the anion coordination chemistry[8] have made the investigation of large polyazacycloalkanes very interesting. Beside these considerations it should be pointed out that dinuclear complexes of synthetic macrocyclic compounds have been extensively studied especially in the solid state.[9] These compounds are interesting from both a theoretical (metal–metal interactions, model system) and practical point of view (catalyst).[10–12] Many different synthetic approaches have been followed in order to obtain dinucleating macrocyclic ligands that can be classified as follows: (i) large monocyclic compounds, with many donor atoms of the same or different kind;[13] (ii) macrocylic subunits linked together;[14] (iii) polycyclic compounds with fused cycles.[15] In the present paper we report the study of a large polyazacycloalkane (hereafter abbreviated as bistrien) with eight secondary nitrogens as donor atoms able to form dinuclear metal complexes. We have studied the copper complex of this macrocycle, its crystal structure, the electrochemical behavior, and the thermodynamics of complex formation.

Experimental Section

Synthesis of the Compounds. All chemicals were reagent grade and were utilized without further purification.

1,4,7,10-Tetrakis(*p*-tolylsulfonyl)-1,4,7,10-tetraazadecane (6).[16] See Figure 1. In a 2-dm^3 three-necked round-bottom flask equipped with mechanical stirrer and condenser, 19 g of 1,4,7,10-tetraazadecane (trien) (0.13 mol) was dissolved in 200 cm^3 of water containing 30 g of NaOH. A solution of 100 g of *p*-tolylsulfonyl chloride (0.53 mol) dissolved in 500 cm^3 of diethyl ether was added dropwise over a period of 6 h, under vigorous stirring. During the addition the reaction mixture was kept at 0 °C and then left at room temperature stirring overnight. The white crude product formed was filtered off, washed with water, ethanol, and diethyl ether, and then recrystallized from a hot methanol and methylene chloride mixture. The product was dried under vacuum at 50 °C: yield 93 g (94%); mp 219–220 °C; TLC[17] one product with R_f 0.52. Anal. Calcd for $C_{34}H_{42}N_4S_4O_8$: C, 53.52; H, 5.55; N, 7.34. Found: C, 53.4; H, 5.5; N, 7.3.

3,6,9,12-Tetrakis(*p*-tolylsulfonyl)-3,6,9,12-tetraazatetradecane-1,14-diol (4). A finely powdered mixture of **6** (53 g, 0.069 mol), ethylene carbonate (12.16 g, 0.138 mol), and potassium hydroxide (0.5 g) was placed in a 1-dm^3 three-necked round-bottom flask equipped with mechanical stirrer, condenser, and thermometer. The stirred mixture was heated on an oil bath until its fusion and then kept at 170 °C for 4 h. The mixture was allowed to cool at 110 °C, and then 500 cm^3 of methanol was rapidly added. The solution was refluxed for 1 h and then cooled at room temperature and stirred overnight. The product obtained was filtered off, dissolved in 1200 cm^3 of methanol and methylene chloride (10:2), and boiled for 30 min in the presence of activated carbon (5 g). The filtered solution was reduced to 600 cm^3 (cloud point) and allowed to cool slowly. The white crude product obtained was filtered, washed with methanol, recrystallized from hot methanol and little methylene chloride, and dried in vacuo at 50 °C: yield 35 g (59%); mp 214–216 °C; TLC one product with R_f 0.71. Anal. Calcd for $C_{38}H_{50}N_4S_4O_{10}$: C, 53.63; H, 5.92; N, 6.58. Found: C, 53.9; H, 5.8; N, 6.6.

***O,O'*-Bis(*p*-tolylsulfonyl)-3,6,9,12-tetrakis(*p*-tolylsulfonyl)-3,6,9,12-tetraazatetradecane-1,14-diol (3).** A solution of **4** (35 g, 0.041 mol) in 200 cm^3 of pyridine was added to a stirred solution of *p*-tolylsulfonyl chloride (16 g, 0.084 mol) in 100 cm^3 of pyridine contained in a 1-dm^3 four-necked round-bottom flask equipped with a mechanical stirrer, condenser, and thermometer. The addition was carried out at 50 °C over 3 h. The cooled solution was added to a vigorously stirred mixture of water and ice (3 dm^3). The white crude product obtained was filtered, washed with water, and recrystallized from hot methanol: yield 41 g (86%); mp 150–152 °C; TLC one product with R_f 0.98. Anal. Calcd for $C_{52}H_{62}N_4S_4O_{14}$: C, 53.87; H, 5.39; N, 4.83. Found: C, 53.9; H, 5.4; N, 4.9.

1,4,7,10,13,16,19,22-Octakis(*p*-tolylsulfonyl)-1,4,7,10,13,16,19,22-octaazacyclotetracosane (2).[18] A solution of **6** (9.5 g, 0.0125 mol) in 1.5 dm^3 of anhydrous DMF was treated with sodium hydride (4 g) in small portions under nitrogen. When the hydrogen evolution was ceased, the solution was filtered in a 3-dm^3 four-necked flask equipped with a mechanical stirrer, condenser, and thermometer, maintaining the nitrogen flux. To this vigorously stirred solution containing the sodium salt **5**, heated at 110 °C, was added a solution of **3** (14.5 g, 0.0125 mol) in 1 dm^3 of anhydrous DMF dropwise over 6 h. The reaction mixture was refluxed for a few hours, reduced at 300 cm^3, and added to a vigorously stirred mixture of water and ice (3 dm^3). The crude product obtained was filtered off, washed with water, and recrystallized a few times from hot methanol and minimum methylene chloride: yield 7.05 g (36%); mp 268–270 °C; TLC one product with R_f 0.87. IR spectra demonstrated that cyclization had occurred since no bands in the N–H region (3060–3500 cm^{-1}) were observed. Anal. Calcd for $C_{72}H_{88}N_8S_8O_{16}$: C, 54.80; H, 5.62; N, 7.10. Found: C, 54.7; H, 5.6; N, 7.1.

1,4,7,10,13,16,19,22-Octaazacyclotetracosane (bistrien). A 2.35-g (0.0015 mol) sample of **2** was dissolved in 20 cm^3 of H_2SO_4 (96%), and the solution was heated at 100 °C on an oil bath for 70 h.[19] A total of

---

(6) Dietrich, B.; Hosseini, M.; Lehn, J. M.; Sessions, R. B. *Helv. Chim. Acta* **1983**, *66*, 1262.

(7) Atkins, T. J.; Richman, J. E.; Dettle, W. F. *Org. Synth.* **1978**, *58*, 86.

(8) Dietrich, B.; Hosseini, M. W.; Lehn, J. M.; Sessions, R. B. *J. Am. Chem. Soc.* **1981**, *103*, 1282. Kimura, E.; Sakonaka, A.; Yatsunami, T.; Kodama, M. *Ibid.* **1981**, *103*, 3041. Kimura, E.; Sakonaka, A. *Ibid.* **1982**, *104*, 4984.

(9) Hoskins, B. F.; Robson, R.; Williams, G. A. *Inorg. Chim. Acta* **1976**, *16*, 121. Coughlin, P. K.; Dewan, J. C.; Lippard, S. J.; Watanabe, E.; Lehn, J. M. *J. Am. Chem. Soc.* **1979**, *101*, 265. Comarmond, J.; Plumere, J.; Lehn, J. M.; Agnus, Y.; Louis, R.; Weiss, R.; Kahn, O.; Badarau, I. *Ibid.* **1982**, *104*, 6330. Yamashita, M.; Ito, H.; Ito, T. *Inorg. Chem.* **1983**, *22*, 2101.

(10) Hay, P. J.; Thilbeault, J. C.; Hoffmann, R. *J. Am. Chem. Soc.* **1975**, *97*, 4884. Crawford, V. H.; Richardson, H. W.; Wasson, J. R.; Hodgson, D. J.; Hatfield, W. E. *Inorg. Chem.* **1976**, *15*, 2107 and references therein. Chauvel, C.; Girerd J. J.; Jeannin, Y.; Kahn, O.; Lavigne, G. *Ibid.* **1979**, *18*, 3015. Kahn, O.; Badarau, I.; Audiers, J. P.; Lehn, J. M.; Sullivan, S. A. *J. Am. Chem. Soc.* **1980**, *102*, 5936 and references therein.

(11) Malmstrom, B. G. *Adv. Chem. Ser.* **1977**, *No. 162*, 173. Tweedle, M. F.; Wilson, L. J.; Garcia, L.; Babcock, G. T.; Palmer, G. *J. Biol. Chem.* **1978**, *253*, 8065.

(12) Herron, N.; Schammel, W. P.; Jackels, S. C.; Grzybowski, J. J.; Zimmer, L. L.; Busch, D. H. *Inorg. Chem.* **1983**, *22*, 1433. Agnus, Y. L. "Copper Coordination Chemistry: Biochemical and Inorganic Perspectives"; Adenine Press: New York, 1983.

(13) Pilkington, N. H.; Robson, R. *Aust. J. Chem.* **1970**, *23*, 2225. Stotz, R.; Stoufer, R. C. *J. Chem. Soc., Chem. Commun.* **1970**, 1682. Casellato, U.; Vigato, P. A.; Fenton, D. E.; Vidali, M. *Chem. Soc. Rev.* **1979**, *8*, 199. Nelson, S. M. *Pure Appl. Chem.* **1980**, *52*, 2461. Mohapatra, B. K.; Sahoo, B. *Indian J. Chem. Sect. A* **1983**, *22*, 494. Agnus, Y.; Louis, R.; Gisselbrecht, J. P.; Weiss, R. *J. Am. Chem. Soc.* **1984**, *106*, 93.

(14) Calverley, M. J.; Dale, J. *J. Chem. Soc., Chem. Commun.* **1981**, 684. Barefield, E. K.; Chueng, D.; Van Derveer, D. G. *Ibid.* **1981**, 302. Buttafava, A.; Fabbrizzi, L.; Perotti, A.; Seghi, B. *Ibid.* **1982**, 1166. Ciampolini, M.; Micheloni, M.; Nardi, N.; Vizza, F.; Buttafava, A.; Fabbrizzi, L.; Perotti, A. *Ibid.*, submitted for publication.

(15) Lehn, J. M.; Pine, S. H.; Watanabe, E.; Willard, A. K. *J. Am. Chem. Soc.* **1977**, *99*, 6766. Lehn, J. M. *Pure Appl. Chem.* **1980**, *52*, 2441.

(16) Hung, Y. *Inorg. Synth.* **1980**, *20*, 106.

(17) TLC measurements were carried out on precoated TLC plates silica gel 60 F-254 (Merk) with a methylene chloride–*n*-esane–methanol (8:4:1) mixture as eluent.

(18) Stetter, H.; Mayer, K. H. *Chem. Ber.* **1961**, *94*, 1410. Simmons, H. E.; Park, C. H. *J. Am. Chem. Soc.* **1968**, *90*, 2428.

Table I. Crystal and Refinement Data

mol formula	$Cu_2C_{16}O_8N_8H_{40}Cl_4$
mol wt	741.44
a, Å	11.811 (2)
b, Å	11.352 (2)
c, Å	11.385 (2)
β, degw	99.11 (3)
V, Å^3	1507.2
Z	2
space gp	$P2_1/m^a$
ρ(calcd), g cm^{-3}	1.64
radiation	graphite monochromated Mo Kα ($\lambda = 0.7107$ Å)
temp, °C	25
μ, cm^{-1}	14.5
scan tech	$\theta/2\theta$
scan speed, deg min^{-1}	3.6
scan width, deg	1.0
scan range, deg	$4.0 < 2\theta < 50.0$
total no. of indep reflcns	2766
no. of obsd reflcns ($F_o > 2\sigma(F_o)$)	1340
no. of refined parameters	175
R,^{b} (F_o)	8.04
R_w,^{c} (F_o)	6.97

[a] Based on centric distribution of E values and later confirmed by the structural determination. [b] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [c] $R_w = [\Sigma_w(|F_o| - |F_c|)^2/\Sigma_w(F_o)^2]^{1/2}$.

100 cm^3 of cooled ethanol in small portions and 100 cm^3 of diethyl ether were added to the solution, and the white crude product obtained was filtered and washed with ethanol. The white product then was dissoved in water (200 cm^3) and eluted through an ionic exchange resin (Dowex 1 × 8). The solution containing the free amine was distilled to dryness under vacuum. The amine was purified as an octahydrochloride; yield 0.60 g (63.3%). Anal. Calcd for $C_{16}H_{48}N_8Cl_8$: C, 30.20; H, 7.60; N, 17.61; Cl, 44.59. Found: C, 30.1; H, 7.6; N, 17.6; Cl, 44.60. ^{13}C NMR spectrum of bistrien·8HCl (water with 15% D_2O, 20 MHz) consists of only one signal at δ 44.4 (CH_2).

Copper Complex. Well-formed crystals of $[Cu_2(bistrien)Cl_2](ClO_4)_2$ used for crystal structure determination were obtained by mixing 0.1 g (0.157 mol) of bistrien·8HCl dissolved in 6.3 cm^3 of 0.2 M NaOH and a water solution (2 cm^3) containing 0.116 g (0.314 mmol) of $Cu(ClO_4)_2 \cdot 6H_2O$. By slow evaporation of the resulting solution at room temperature deep blue crystals of the above complex grew. The product was filtered off, washed with ethanol, and dried in vacuo at 50 °C. Anal. Calcd for $C_{16}H_{40}N_8O_8Cu_2Cl_4$: C, 25.91; H, 5.43; N, 15.11. Found: C, 26.0; H, 5.4; N, 15.0. The magnetic moment of the complex, measured by the Faraday method, resulted to be $\mu_{eff} = 2.81\ \mu_B$ at 298 K.

Materials. All potentiometric and calorimetric measurements were carried out in 0.5 mol dm^{-3} $NaClO_4$ (C. Erba ACS grade) purified according to the procedure already described.[20] Standardized CO_2-free solutions of NaOH, used in the potentiometric and calorimetric experiments, were prepared following the procedure described in ref 21.

Emf Measurements. The potentiometric titration was carried out by using equipment (potentiometer, buret, stirrer, thermostated cell, microprocessor, etc.) that has been already fully described.[22] The new computer program SUPERQUAD[23] was used to process data and calculate both basicity and stability constants.

Calorimetric Measurements. For the calorimetric measurements the LKB BATCH Model 10700-2 microcalorimeter was used. The direct reaction between Cu(II) and bistrien is fast; the heat of reaction was measured by mixing an aqueous solution of Cu(II) with a solution of the macrocycle bistrien containing a slight excess of NaOH. The species present and their percentages were calculated at equilibrium before and after mixing under the reaction conditions used in the calorimeter and employing the stability constants determined. The only significant species present at equilibrium before and after mixing were the free nonprotonated ligand and the complex Cu_2bistrien, respectively. Corrections for the enthalpy of dilution of NaOH–bistrien solutions were made for each measurement.[24]

Table II. Positional Parameters and Their Estimated Standard Deviations in Parentheses (×10^4)

atom	x/a	y/b	z/c
Cu(1)	2001 (1)	4631 (2)	2041 (2)
N(1)	411 (8)	5251 (10)	2360 (8)
N(2)	2415 (10)	4649 (13)	3840 (10)
N(3)	3710 (9)	4831 (11)	2101 (9)
N(4)	1920 (8)	4971 (9)	271 (8)
C(1)	−687 (10)	4807 (14)	1704 (11)
C(2)	450 (11)	5199 (17)	3670 (10)
C(3)	1634 (12)	5494 (15)	4287 (13)
C(4)	3647 (11)	4887 (16)	4184 (14)
C(5)	4127 (12)	5504 (17)	3191 (12)
C(6)	3900 (11)	5419 (17)	992 (12)
C(7)	3107 (10)	4859 (15)	−016 (11)
C(8)	1075 (10)	4394 (11)	−606 (11)
Cl(1)	1725 (5)	7500 (0)	1557 (5)
Cl(2)	1547 (5)	2500 (0)	1854 (5)
Cl(3)	7604 (7)	7500 (0)	3474 (7)
Cl(4)	3836 (6)	7500 (0)	7409 (8)
O(1)	8196 (22)	7500 (0)	4679 (25)
O(2)	8614 (25)	7500 (0)	2861 (26)
O(3)	7161 (16)	6457 (18)	3241 (17)
O(4)	4898 (23)	7500 (0)	8112 (26)
O(5)	3062 (32)	7500 (0)	8193 (35)
O(6)	3735 (19)	6405 (16)	6885 (21)
O(4′)	4495 (43)	7500 (0)	6514 (38)
O(5′)	4619 (39)	7500 (0)	8448 (31)
O(6′)	3334 (20)	6404 (16)	7358 (23)

Table III. Basicity Constants of Bistrien in Aqueous Solution (25 °C in 0.5 mol dm^{-3} $NaClO_4$ (Standard State 1 mol dm^{-3}) and [32]aneN_8^{a})

	bistrien	[32]ane N_8^{a}		bistrien	[32]ane N_8^{a}
log K_1	10.01 (1)^b	10.65	log K_6	3.71 (1)	7.55
log K_2	9.50 (2)	10.55	log K_7	2.98 (2)	6.85
log K_3	9.10 (2)	9.70	log K_8	1.97 (4)	6.50
log K_4	8.29 (1)	9.20	log β_8	50.57	69.20
log K_5	5.01 (1)	8.20			

[a] Taken from ref 6; in aqueous solution at 25 °C $I = 0.1$ mol dm^{-3} (NaTs). [b] Values in parentheses are standard deviations in the last significant figure.

Spectrophotometric Measurements. Electronic spectra were recorded on a Beckman DK2-A spectrophotometer in the solid state and on a Varian Cary Model 17 spectrophotometer in solution.

Electrochemical Measurements. Electrochemical analysis by cyclic voltammetry involved the use of an electrochemical unit (Amel Model 552 potentiostate with an Amel Model 862/A pen recorder) and of a classical three-electrode cell.[25] The working electrode was a platinum microsphere, the auxiliary electrode was a platinum disk and the reference was a calomel electrode in aqueous saturated KCl (SCE). Before each experiment the solution was carefully deoxygenated with a nitrogen flow.

Collection and Reduction of X-ray Intensity Data. A blue needlelike crystal with approximate dimensions 0.04 × 0.05 × 0.60 mm was mounted on a Philips PW 1100 computer-controlled diffractometer and used for data collection. A summary of the crystallographic data is reported in Table I. Unit-cell dimensions were determined from the angular settings of 23 carefully centered reflections. Intensities were corrected for Lorentz, polarization, and absorption effects[26] (transmission factors ranged between 0.91 and 0.95). The intensities of three standard reflections were monitored periodically for stability control during data collection.

Solution and Refinement of the Structure. The structure was solved by the heavy-atom technique, with the use of Patterson and electron density syntheses. Refinement was performed by means of the full-matrix least-squares method. The function minimized was $\sum_w (|F_o| - |F_c|)^2$

---

(19) Smith, W. L.; Ekstrand, J. D.; Raymond, K. N. *J. Am. Chem. Soc.* **1978**, *100*, 3539.

(20) Micheloni, M.; May, P. M.; Williams, D. R. *J. Inorg. Nucl. Chem.* **1978**, *40*, 1209.

(21) Micheloni, M.; Sabatini, A.; Vacca, A. *Inorg. Chim. Acta* **1977**, *25*, 41.

(22) Bianchi, A.; Bologni, L.; Dapporto, P.; Micheloni, M.; Paoletti, P. *Inorg. Chem.* **1984**, *23*, 1201.

(23) Gans, P.; Sabatini, A.; Vacca, A. *Inorg. Chim. Acta* **1983**, *79*, 219.

(24) Anichini, A.; Fabbrizzi, L.; Paoletti, P.; Clay, R. M. *J. Chem. Soc., Chem. Commun.* **1977**, 244.

(25) Sawyer, D. T.; Roberts, J. L. "Experimental Electrochemistry for Chemist"; Wiley: New York, 1974.

(26) Sheldrick, G. M. "SHELX-76, Program for Crystal Structure Determination"; University of Cambridge: Cambridge, England, 1976.

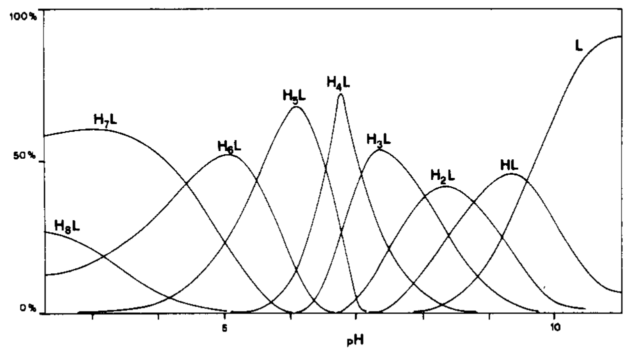

Figure 2. Distribution diagram for the system H^+–bistrien (charges omitted).

with weights $w = a/(\sigma^2(F) + bF^2)$, where a and b are adjustable parameters. Anisotropic thermal parameters were refined for all non-hydrogen atoms except the perchlorate oxygen atoms. Hydrogen atoms were included in calculated positions, and their parameters were not refined. The refinement of the perchlorate ions, which exhibited high thermal motion and some rotational disorder, gave some problems. For one of them, better results were obtained by fitting two slightly rotated tetrahedral models with a unique Cl–O distance and O–Cl–O angle. The site occupation factor resulted very close to 0.33 and 0.66, respectively, for the two models. A final difference Fourier synthesis showed only some diffuse peaks (less than 1 e/A^3) in the zone of perchlorate ions. All the calculations were performed with the SHELX-76 set of programs[26] that use the analytical approximation for the atomic scattering factors and anomalous dispersion corrections for all the atoms from ref 27. Table II reports the list of the final atomic coordinates for non-hydrogen atoms with estimated standard deviations obtained from the least-squares inverse matrix. The molecular plots were produced by the program ORTEP.[28]

Results and Discussion

Protonation. The stepwise protonation constants for bistrien have been reported in Table III. For comparison, the protonation constants for the similar polyazacycloalkane [32]aneN_8 have been also reported.[6] The results show that the macrocycle bistrien behaves as strong base in the first four steps of protonation and as much weaker base in the last four steps of protonation. This grouping of the basicity constants is always present in polyazacycloalkanes.[22,29] This behavior can be ascribed to the electrostatic repulsions among the positive charges on the protonated cyclic polyamines, and it is much more marked for smaller polyazacycloalkanes.[30] As expected, the macrocycle bistrien is less basic than the larger macrocycle [32]aneN_8 in each step of protonation. In the last macrocycle, where the nitrogen atoms are bridged by propylene chains, the positive charges of the protonated forms are more far away than in bistrien in which each hydrocarbon chain is made by only two carbon atoms. As shown by the distribution diagram for the system H^+–bistrien (see Figure 2) in the neutral pH region many highly charged species are present, making bistrien a promising ligand for anion coordination chemistry.

Description of the Structure of $[Cu_2(bistrien)Cl_2](ClO_4)_2$. The structure of the compound consists of centrosymmetric binuclear Cu_2(bistrien) units, connected by ···Cu–Cl–Cu···Cl···Cu–chains running along the *b* axis. In the binuclear unit each copper atom is coordinated by four nitrogen atoms of the macrocyclic ligand and one chloride ion, forming a distorted square pyramid (Figure 3). The nitrogen atoms lie approximately in the basal plane with a maximum deviation of 0.14 Å from the least-squares plane through them. The copper atom is 0.36 Å out of the plane. A further chloride ion at 3.31 (1) Å from the copper atom completes a distorted elongated octahedron. Bond lengths and angles around the copper atom and in the rest of the molecule are reported in Table IV. The mean Cu–N distance of 2.04 (1) Å is in agreement with analogous distances in five-coordinated Cu(II) complexes.[31] The Cu–Cl(2) distance (2.48 (1) Å) is close to the apical Cu–Cl bond length (2.453 (1) Å) in the binuclear [24]aneN_2S_4 copper complex as found by Agnus et al.[13] The intramolecular copper–copper distance is 6.138 (1) Å.

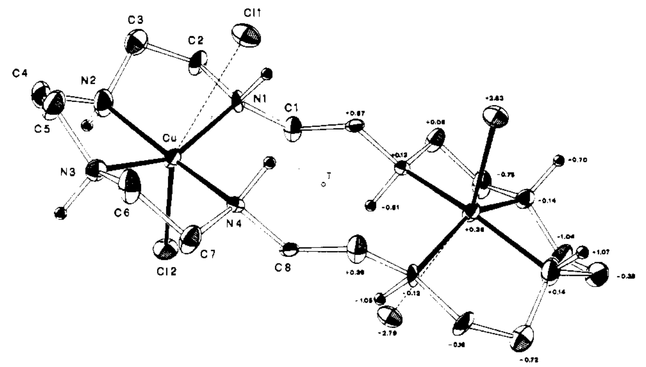

Figure 3. View of the monomeric $Cu_2(bistrien)Cl_4$ unit showing the atom labeling and the deviations of the atoms from the least-squares plane through the four basal nitrogen atoms of the coordination square pyramid. Thermall ellipsoids are drawn at 30% probability. Only the hydrogen atoms attached to the nitrogen atoms are shown as spheres of arbitrary radius.

Table IV. Interatomic Distances (Å) and Angles (deg) with Estimated Standard Deviations in Parentheses

Distances			
Cu-N(1)	2.09 (1)	C(5)-N(3)	1.47 (2)
Cu-N(2)	2.03 (1)	N(3)-C(6)	1.48 (2)
Cu-N(3)	2.02 (1)	C(6)-C(7)	1.50 (2)
Cu-N(4)	2.04 (1)	C(7)-N(4)	1.49 (1)
Cu-Cl(2)	2.48 (1)	N(4)-C(8)	1.45 (1)
Cu···Cl(1)	3.31 (1)	C(1)-C′(8)	1.57 (1)
N(1)-C(1)	1.48 (2)	Cl(3)-O(1)	1.44 (3)
N(1)-C(2)	1.48 (2)	Cl(3)-O(2)	1.47 (3)
C(2)-C(3)	1.50 (2)	Cl(3)-O(3)	1.31 (2)
C(3)-N(2)	1.48 (2)	Cl(4)-O[a]	1.38 (2)
N(2)-C(4)	1.47 (2)	Cu-Cu[b]	6.138 (2)
C(4)-C(5)	1.51 (2)		

Angles			
N(1)-Cu-N(2)	84.3 (4)	C(3)-N(2)-Cu	106.9 (9)
N(2)-Cu-N(3)	83.4 (4)	C(3)-N(2)-C(4)	115.8 (13)
N(3)-Cu-N(4)	84.4 (4)	C(4)-N(2)-Cu	109.9 (9)
N(1)-Cu-N(4)	101.8 (4)	N(2)-C(4)-C(5)	110.9 (12)
N(1)-Cu-Cl(2)	98.9 (4)	C(4)-C(5)-N(3)	105.9 (13)
N(2)-Cu-Cl(2)	96.3 (5)	C(5)-N(3)-Cu	106.6 (8)
N(3)-Cu-Cl(2)	108.3 (4)	C(5)-N(3)-C(6)	114.2 (12)
N(4)-Cu-Cl(2)	97.1 (3)	C(6)-N(3)-Cu	107.9 (8)
N(1)-Cu-N(3)	151.2 (5)	N(3)-C(6)-C(7)	107.5 (13)
N(2)-Cu-N(4)	164.1 (5)	C(6)-C(7)-N(4)	106.9 (11)
C(2)-N(1)-Cu	105.9 (8)	C(7)-N(4)-Cu	107.5 (7)
C(1)-N(1)-Cu	122.5 (8)	C(7)-N(4)-C(8)	112.2 (10)
C(1)-N(1)-C(2)	112.3 (10)	C(8)-N(4)-Cu	121.0 (8)
N(1)-C(2)-C(3)	109.9 (11)	N(4)-C(8)-C(1)′	111.3 (9)
C(2)-C(3)-N(2)	106.3 (13)	N(1)-C(1)-C(8)′	109.0 (10)
		O-Cl(4)-O[a]	105.1 (6)
		O(1)-Cl(3)-O(2)	98.2 (16)
		O(1)-Cl(3)-O(3)	108.2 (10)
		O(2)-Cl(3)-O(3)	103.4 (10)

[a] A unique Cl-O distance and O-Cl-O angle were refined for this ion. [b] This is the distance between the copper atoms within the ring.

Bond lengths and angles in the macrocyclic ring are in agreement with literature values. The ring has a chair-shaped configuration, with all five-membered chelate rings in the gauche

---

(27) "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV.

(28) Johnson, C. K. "ORTEP", Report ORNL-3794; Oak Ridge National Laboratory: Oak Ridge, TN, 1971.

(29) Micheloni, M.; Paoletti, P.; Vacca, A. *J. Chem. Soc., Perkin Trans. 2* **1978**, 945. Micheloni, M.; Paoletti, P.; Sabatini, A. *Ibid.* **1978**, 828. Bartolini, M.; Bianchi, A.; Micheloni, M.; Paoletti, P. *Ibid.* **1982**, 1345.

(30) Leugger, A. P.; Hertli, L.; Kaden, T. A. *Helv. Chim. Acta* **1978**, *61*, 2296.

(31) Clay, R. M.; Rust, P. M.; Rust, J. M. *Acta Crystallogr. Sect. B: Struct. Crystallogr. Cryst. Chem.* **1979**, *B35*, 1894.

Table V. Thermodynamic Parameters of Formation of Cu(II) Complexes with bistrien in Aqueous Solution (25 °C in 0.5 mol dm^{-3} $NaClO_4$ (Standard State 1 mol dm^{-3}))

reaction	log *K*	$-\Delta G^{\ominus}$, kcal mol^{-1}	$-\Delta H^{\ominus}$, kcal mol^{-1}	$T\Delta S^{\ominus}$, kcal mol^{-1}
$2Cu^{2+} + bistrien \rightleftarrows [Cu_2(bistrien)]^{4+}$	36.63 (3)	49.96 (4)	39.0 (5)	11.0 (5)
$2Cu^{2+} + 2H^+ + bistrien \rightleftarrows [Cu_2(bistrien)H_2]^{6+}$	42.02 (4)			
$[Cu_2(bistrien)]^{4+} + 2H^+ \rightleftarrows [Cu_2(bistrien)H_2]^{6+}$	5.39			
$2Cu^{2+} + [(bistrien)H_2]^{2+} \rightleftarrows [Cu_2(bistrien)H_2]^{6+}$	22.51			
$2Cu^{2+} + H_2O + bistrien \rightleftarrows [Cu_2(bistrien)OH]^{3+} + H^+$	26.12 (4)			
$[Cu_2(bistrien)]^{4+} + OH^- \rightleftarrows [Cu_2(bistrien)OH]^{3+}$	3.21			

configuration. This is similar to what found in (nitrato)-(1,4,7,10-tetraazacyclododecane)copper(II) nitrate,[31] with the interesting difference of the orientation of the hydrogen atoms attached to the nitrogen atoms (Figure 3), which are all on the same side of the apical ligand in the mononuclear complex.[31]

The crystal packing of the present compound appears quite interesting (see supplementary material). The binucleating macrocyclic ring packing layers are perpendicular to the *b* axis, alternating with layers of chloride and perchlorate ions. The layers containing the rings are mirror related by symmetry planes passing through the chloride and the perchlorate anions. In the zigzag-shaped ···Cu–Cl–Cu···Cl···Cu– chains, each copper atom forms one short (2.48 (1) Å) and one long (3.31 (1) Å) bond. However, it is interesting to point out that the distances of the chloride ions from the least-squares plane through the nitrogen atoms are the same within the standard deviations (2.79 (2), 2.83 (2) Å).

The bond angles in the chains are Cl(1)···Cu–Cl(2) = 158.1 (2)°, Cu–Cl(2)–Cu = 154.6 (2)°, and Cu···Cl(1)···Cu = 159.3 (2)°. The perchlorate oxygen atoms are hydrogen bonded to the ring nitrogen atoms, the shortest distances being N(2)···O(1) = 3.11 Å and N(3)···O(1) = 3.14 Å.

Copper(II) Complexes. The results for $\Delta G^{\ominus}$ (log *K*) for the copper(II) complexes with bistrien and enthalpy of formation ($\Delta H^{\ominus}$) of $[Cu_2(bistrien)]^{4+}$ are given in Table V. The study of the formation equilibria of the Cu(II) complexes with the bistrien macrocycle points out the following characteristics: (i) the relative simplicity of the system with only three species $[Cu_2(bistrien)]^{4+}$, $[Cu_2(bistrien)H_2]^{6+}$, and $[Cu_2(bistrien)OH]^{3+}$; (ii) the presence of the dinuclear species $[Cu_2(bistrien)]^{4+}$ extremely stable and by far the most important species in the investigated pH range; (iii) the absence of the mononuclear species $[Cu(bistrien)]^{2+}$. Also a considerable exothermicity is associated with the large stability of the dinuclear species $[Cu_2(bistrien)]^{4+}$, as it is shown by the enthalpy changes. To our knowledge this is the first enthalpy of formation of dinuclear complexes of polyazacycloalkanes so far published. The enthalpy of formation of $[Cu_2(bistrien)]^{4+}$ is high and comparable to the one that is obtained doubling the enthalpy of formation of the complex with the linear ω,ω'-dimethylated tetraamine 3,6-diaza-1,8-diaminooctane (Me_2trien) ($Cu + Me_2trien \rightleftarrows Cu(Me_2trien)$; $-\Delta H^{\ominus} = 21.1$ kcal mol^{-1}).[32] Everything is consistent with the fact that bistrien has a great capacity of coordinating two Cu(II) ions wigh all its donor atoms, as shown also in the solid-state structure. The aqueous solution of the complex $[Cu_2(bistrien)]^{4+}$ shows a wide absorption band at 16600 cm^{-1} ($\epsilon = 380$ dm^3 mol^{-1} cm^{-1}). The spectrum was essentially the same as in the solid state. A more detailed analysis of the equilibria of formation of the two species $[Cu_2(bistrien)H_2]^{6+}$ and $[Cu_2(bistrien)OH]^{3+}$ allows for some considerations. The formation of protonated species presupposes, in the case of polyaza macrocycle complexes, the breakage of one –M–N bond and the formation of one $-N-H^+$ type bond. The total process will be the more unfavorable the stronger the M–N bond. The dinuclear complex has a poor tendency to protonate itself as shown by the equilibrium constant corresponding to the addition of two protons to the complex (see Table V). This constant is much smaller than the one relating to the protonation of the first nitrogen in the free macrocycle (see Table III). We can compare the equilibrium constants between two copper ions and the diprotonated ligand $[H_2bistrien]^{2+}$ (see Table V) with that between two copper ions and the macrocycle bisdien reported in ref 33, the donor atom set being N_6O_2 in the latter case. The logarithms for these constants are comparable, being 22.51 (see Table V) and 27.2, respectively. The two ligands are of comparable size, and in both equilibria there are six unprotonated nitrogen atoms involved in the coordination to the metal ions. The difference in stability, which is not large, can be partially explained in terms of charge repulsions between metal ions and ligand, since $[H_2bistrien]^{2+}$ is doubly charged and bisdien neutral. The presence of only the diprotonated species reveals the "symmetric" behavior of the dinuclear complex. This kind of behavior is not found, on the other hand, in the formation of the hydroxo species $[Cu_2(bistrien)OH]^{3+}$, which contains only one OH^- group. It is worth noting that in the formation equilibria of mononuclear species between the Cu(II) ion and polyazacycloalkanes the formation of hydroxo species is very rare. In our case, instead, the hydroxo species is formed and is also very stable as demonstrated by the equilibrium constant relative to the addition of the hydroxide ion to the dinuclear complex (log *K* = 3.21) (see Table V). The magnetic susceptibility of the dinuclear complex, measured in solution by the Evans method[34] on a Varian CFT 20 spectrometer at pH 4.6, which

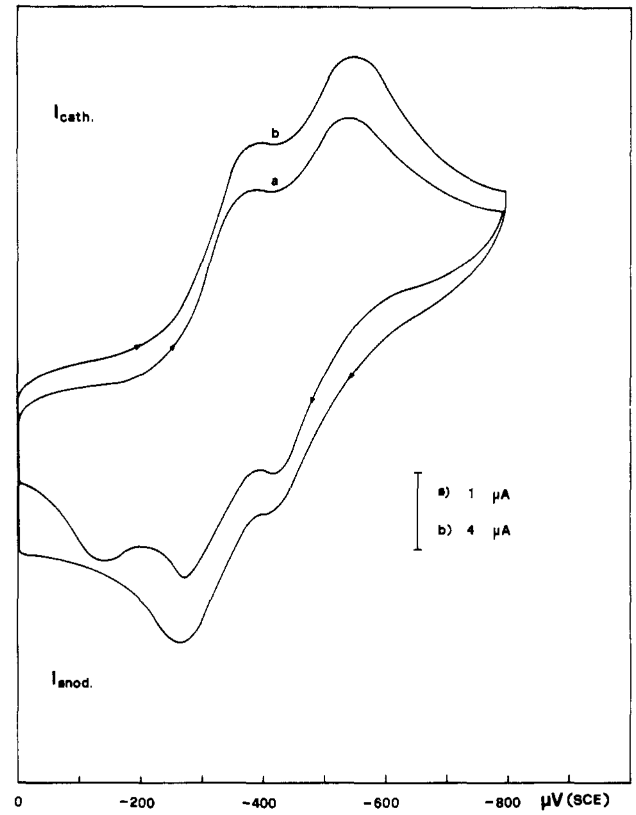

Figure 4. Cyclic voltammetry curves recorded on an aqueous solution containing $[Cu_2(bistrien)]^{4+}$ (10^{-4} mol dm^{-3}) with a platinum microsphere as working electrode. Scan rates: (a) 10 mV s^{-1}; (b) 200 mV s^{-1}.

---

[32] Clay, R. M.; McCormac, H.; Micheloni, M.; Paoletti, P. *Inorg. Chem.* **1982**, *21*, 2494.

[33] Motekaitis, R. J.; Martell, A. E.; Lecomte, J. P.; Lehn, J. M. *Inorg. Chem.* **1983**, *22*, 609.

[34] Evans, D. F. *J. Chem. Soc.* **1959**, 2003.

excludes the presence of the hydroxo species, is similar to that of the solid complex. The susceptibility lowers significantly on increasing the pH and the hydroxo species concentration. In conclusions, the formation of the monohydroxo species, its high formation constant, and its influence on the magnetic susceptibility are experimental evidence that make reasonable the hypothesis that this species has the hydroxide ion bridging the two metal ions with consequent increasing of the metal–metal interaction.

Electrochemical Studies. An aqueous solution of the [Cu$_2$(bristrien)]$^{4+}$ complex has been investigated by using the CV technique. At a potential scan rate of 200 mV s^{-1} for higher the current/potential profile shows two consecutive peaks in reduction, followed, in the reversed scan, by two oxidation peaks (see Figure 4). The separation between the peaks, more evident in the reduction scan, is about 150 mV. The peaks do not shift on the potential axis as a function of scan rate. The intensity of each peak, in comparison with a monoelectronic standard (e.g., [Ni(cyclam)](ClO$_4$)$_2$[35]) would correspond to the addition of 1 e. Thus, the dinuclear species [Cu$_2$(bistrien)]$^{4+}$ presents a behavior corresponding to a two-electron reversible reduction into the dinuclear Cu(I) species, by two independent monoelectronic steps. It is worth observing that for a potential scan rate lower than 200 mV s^{-1} an anodic peak appears in the oxidation scan at ca. −145 mV whose intensity increases with the decreasing of the scan rate (see Figure 4). Such a peak should be ascribed to the anodic stripping due to the oxidation of deposited copper metal.[36] In fact, during the controlled-potential electrolysis at the potential of the second peak of reduction (−525 mV), deposition of the copper metal on the surface of the platinum electrode was observed. All this evidence suggests that the [Cu$^{I}_2$(bistrien)]$^{2+}$ species is unstable with respect to the disproportionation by which copper metal is produced. Such behavior, already observed in mononuclear complexes of Cu(II) and tetraaza macrocycles,[37] is justified by the instability of the binuclear cuprous species.

Acknowledgment. We thank P. Innocenti for recording NMR spectra and the ISSECC Institute for computing and crystal data collection facilities. Financial support from Progetto Finalizzato Chimica Fine e Secondaria of the Italian Research Council (CNR) is gratefully acknowledged.

Registry No. 1·8HCl, 94957-30-9; **2**, 94957-31-0; [Cu$_2$(bistrien)Cl$_2$](ClO$_4$)$_2$, 94957-29-6.

Supplementary Material Available: Listings of observed and calculated structure factors, thermal parameters, and hydrogen atom coordinates and a stereoview of the crystal packing of the title compound (11 pages). Ordering information is given on any current masthead page.

---

(35) Sabatini, L.; Fabbrizzi, L. *Inorg. Chem.* **1979**, *18*, 438.

(36) Zanello, P.; Fabbrizzi, L.; Seeber, R.; Cinquantini, A.; Mazzocchin, G. A. *J. Chem. Soc., Dalton Trans.* **1982**, 893.

(37) Fabbrizzi, L.; Lari, A.; Poggi, A.; Seghi, B. *Inorg. Chem.* **1982**, *21*, 2083.

Contribution from the Departamento de Quîmica Inorgânica, Facultad de Ciencias,
Universidad de Mâlaga, Mâlaga, Spain 29004

Intercalation of Polar Organic Compounds into Sn(HPO$_4$)$_2$·H$_2$O

ENRIQUE RODRÎGUEZ-CASTELLÔN,* AURORA RODRÎGUEZ-GARCIA, and SEBASTIAN BRUQUE

Received May 8, 1984

Several types of amines and amides, and dimethyl sulfoxide, were intercalated in the layered structure of tin(IV) hydrogen phosphate hydrate (Sn(HPO$_4$)$_2$·H$_2$O). Pyridine, 4,4′-bipyridine, and dimethyl sulfoxide form a monolayer, while piperidine, aniline, *m*-toluidine, and 3,5-dimethylaniline form a bilayer. The stoichiometry is governed by the "covering effect". A qualitative study of this phenomenon is reported for pyridine. Many quest molecules suitable for layered host structure (urea, thiourea, and formamide) do not intercalate. However, a slightly more basic molecule such as *N,N*-dimethylformamide does. The thermal decomposition of the resulting intercalates takes place in three stages: dehydration, removal of the organic molecule, and condensation of the hydrogen phosphate to pyrophosphate.

Introduction

Crystalline tin(IV) hydrogen phosphate (α-SnP) possesses a layered lattice structure similar to that of zirconium(IV) hydrogen phosphate (α-ZrP).[1-3] The metal atoms lie nearly in a plane; they are bridged by phosphate groups. Three oxygens of each phosphate are linked to three tin atoms. Each metal atom is thus octahedrally coordinated by oxygen. The fourth oxygen of each phosphate group bears a proton. The interlayer distance is 7.8 Å.

Very little work has been done on the intercalation chemistry of α-SnP. Michel and Weiss[4] showed that α-SnP undergoes unidimensional swelling when contacted with octylamine, dioctylamine, and trioctylamine. In a previous paper,[5] we reported the formation of complexes between *n*-alkylamines and α-SnP. The intercalation chemistry of layered phosphates has become important as a result of the better understanding of the structure and properties of these compounds.

Experimental Section

Preparation of Tin(IV) Hydrogen Phosphate. To 1 L of 8 M H$_3$PO$_4$ and 3 M HNO$_3$ was added a solution of anhydrous tin(IV) chloride, until the P:Sn ratio was 30. Although the precipitation was complete in 2 days, refluxing was continued for ~150 h. After refluxing, the material was washed with distilled water and then batch treated with 1 M HNO$_3$ to ensure complete conversion to the H$^+$ form. The material was again washed with distilled water to a pH of 3.4–4.0, separated by centrifuge, and then air dried.[6,7] The chemical composition was determined by dissolving the phosphate in 1 M NaOH. The phosphate content was determined colorimetrically.[8] Tin(IV) was determined by precipitation with cupferron and calcination to SnO$_2$.[9] Water was determined by thermogravimetric analysis. Anal. Calcd for Sn(HPO$_4$)$_2$·H$_2$O: SnO$_2$, 45.85; P$_2$O$_5$, 43.19; H$_2$O, 10.96. Found: SnO$_2$, 46.99; P$_2$O$_5$, 41.87; H$_2$O, 11.29.

---

(1) Chernorukow, N. G.; Mochalova, I. R.; Moscuichev, E. P.; Sibrina, G. B. *Zh. Prikl. Khim.* (*Leningrad*) **1977**, *50*, 1618.

(2) Clearfield, A.; Smith, G. D. *Inorg. Chem.* **1969**, *8*, 431.

(3) Troup, J. M.; Clearfield, A. *Inorg. Chem.* **1977**, *16*, 331.

(4) Michel, E.; Weiss, A. *Z. Naturforsch., B: Anorg. Chem. Org. Chem., Biochem., Biophys., Biol.* **1965**, *20B*, 1307.

(5) Rodrîguez-Castellôn, E.; Bruque, S.; Rodrîguez-Garcia, A. *J. Chem. Soc., Dalton Trans.* **1985**, 213.

(6) Costantino, U.; Gasperoni, A. *J. Chromatogr.* **1970**, *51*, 289.

(7) Fuller, M. J. *J. Inorg. Nucl. Chem.* **1971**, *33*, 559.

(8) Alberti, G.; Cardini-Galli, P.; Costantino, U.; Torraca, E. *J. Inorg. Nucl. Chem.* **1967**, *29*, 571.

(9) Heyn, A. H.; Dove, N. G. *Talanta* **1966**, *13*, 33.