Synthesis and Structure of Chiral Metal Complexes of Polyazacycloalkane Ligands Incorporating Phosphinic Acid Donors

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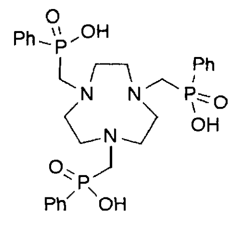
The chiral copper(II) and gallium(III) complexes of a triazatris(phenylphosphinic acid) ligand have very similar structures: the anionic copper complex possesses C_3 symmetry, shows no Jahn–Teller distortion at 293 K nor at 123 K and is resistant to protonation.

Aminoalkylphosphinic acids are intriguing complexing agents that possess distinct differences in their behaviour from their carboxylic acid analogues. The pentavalency of phosphorus means that the alkyl (or aryl) substituent on the phosphorus atom may be used to allow further ligand functionalisation. In addition, when the phosphinic acid oxygen is coordinated to a metal atom, a new stereogenic centre at phosphorus is created and stereoisomeric complexes may form. A phosphinic acid is usually more acidic than the corresponding carboxylic acid so that protonation on oxygen in both the ligand and in the complex occurs only under strongly acidic conditions. The polyaza-macrocyclic complexing agents **1**, **2**, and **3**, **4** are hexadentate and octadentate ligands representative of this class of complexing agent.[1,2] Their structural and chemical properties underline the importance of these distinctive features.

The phenylphosphinic acids **1** and **4** were prepared by reaction of 1,4,7-triazacyclononane or 1,4,7,10-tetraazacyclododecane with paraformaldehyde and $PhP(OMe)_2$ in tetrahydrofuran (THF), followed by acidic hydrolysis (6 mol dm^{-3}



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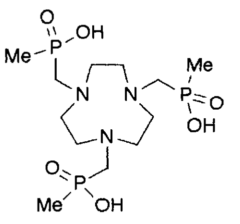

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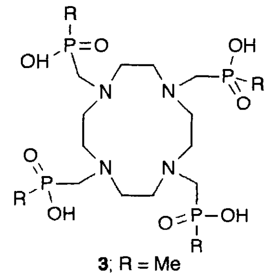

3; R = Me
4; R = Ph

Table 1 Protonation constants and ^{31}P NMR data for ligands **1** to **4**[a] (298 K, $I = 0.1$, Me_4NNO_3)

Ligand	pK_{a_1}[b]	pK_{a_2}	pK_{a_3}		δ_P
1	11.7(1)	6.66(02)	3.68(03)		27.4 (CD_3OD)
2	12.1(2)	7.76(02)	3.75(03)		50.0 (pD O)
3	11.3(1)	8.12(03)	3.66(02)		39.2 (pD 14)
4	11.7(2)	7.44(03)	6.23(01)	2.28(02)	28.9 (pD 13)

[a] Determined by pH-metric titration with data analysis by SCOGS-2 followed by SUPERQUAD. [b] Determined by ^{31}P NMR (ref. 85% H_3PO_4).

HCl, 110 °C, 15 h). Protonation equilibria and ^{31}P NMR data for these ligands and their P–Me analogues, **2** and **3**, are summarised in Table 1. Reaction of **1** with cupric perchlorate in aqueous solution (pH 1.5) led to formation of a blue complex, $[H_3O^+][Cu{\cdot}\mathbf{1}]^-{\cdot}4H_2O$ [$\lambda_{max}(H_2O)$ 700 nm (82 dm^3 mol^{-1} cm^{-1})] whose visible spectrum was essentially invariant in the pH range 2.5 to 10. The crystal structure† of the complex at 293 K revealed that the complex anion possessed C_3-symmetry that was crystallographically imposed (Fig. 1), with *RRR* and *SSS* enantiomers in equal occupancy in the unit cell. The H_3O^+ counterion was remote from the copper atom and involved in a hydrogen-bonded network to other water molecules. The structural analysis at 123 K showed that the complex crystallised in the same space group and no significant structural changes were observed, neither in Cu–O nor Cu–N bond lengths nor in the anisotropy of the thermal parameters for the bound N and O atoms. The absence of a Jahn–Teller distortion at both temperatures is striking[3] for this hexacoordinate d^9 CuN_3O_3 anion, and contrasts with the behaviour of the tris-acetate analogue (NOTA)[4] for which one elongated Cu–N and Cu–O bond was observed and in which reversible protonation on oxygen occurred at pH 2.77.[5] The copper complex anion also possesses a 'helical' element of chirality: the sense of the 'twist' (as seen in the relative position of the N(1)–C(4)–P bonds in Fig. 1) is left handed for the *RRR* enantiomer, and right handed for the *SSS*.

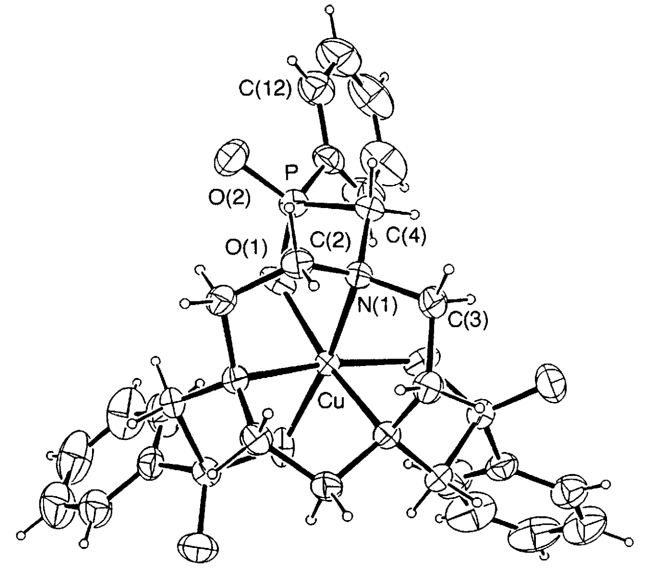

Fig. 1 View down the C_3 axis of $[Cu{\cdot}\mathbf{1}]^-$ in the crystal. Selected bond lengths (Å) and bond angles (°): Cu–N(1) 2.134(3), Cu–O(1) 2.099(3); O(1)–Cu–O(1*) 95.06(9), O(1)–Cu–N(1) 85.90(11), N(1)–Cu–N(1*) 83.10(13).

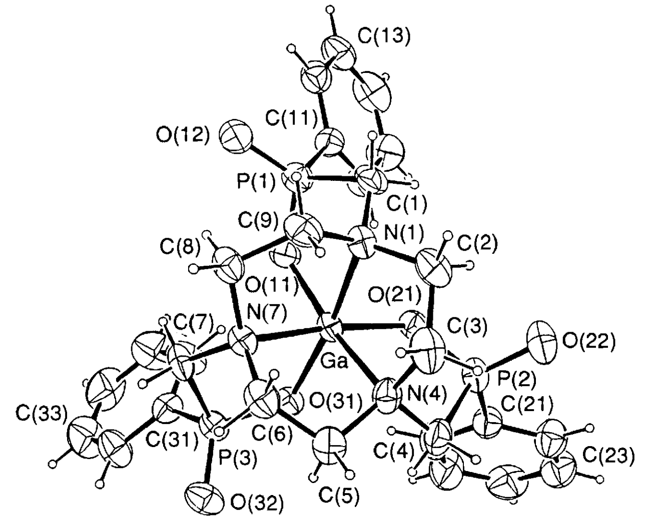

Fig. 2 Structure of [Ga·**1**] in the crystal. Selected bond lengths (Å) and bond angles (°): Ga–N(1) 2.146(5), Ga–N(4) 2.121(7), Ga–N(7) 2.139(5), Ga–O(11) 1.917(4), Ga–O(21) 1.908(4), Ga–O(31) 1.911(4) Å, N(1)–Ga–N(7) 82.0(2), O(11)–Ga–N(1) 86.1(2), O(11)–Ga–O(21) 96.2(2)°.

Complexation of **1** with gallium nitrate in aqueous solution (pH ~ 2) led to crystallisation of a colourless complex $[Ga{\cdot}\mathbf{1}]{\cdot}5H_2O$ and crystallographic analysis‡ (Fig. 2) revealed

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† *Crystal data* for $H_3O^+[Cu{\cdot}\mathbf{1}]{\cdot}4H_2O$. $C_{27}H_{44}CuN_3O_{11}P_3$, $M = 743.1$, trigonal, space group $P\bar{3}$, $a = 14.399(3)$, $c = 9.023(2)$ Å, $U = 1620.0(4)$ Å^3, $Z = 2$, $D_c = 1.522$ g cm^{-3}, $F(000) = 778$, μ(Mo-Kα) = 8.8 cm^{-1}. Intensity data were measured at 20 °C using an Enraf-Nonius CAD4 diffractometer. Lorentz, polarisation and absorption corrections were applied to the data; 3893 reflections were measured of which 2360 were unique and the 1254 with $I > 3(\sigma)$ were labelled observed and used in the structural study. The structure was solved by the heavy atom method and refined by full-matrix least-squares calculations. At convergence $R = 0.040$, $R_w = 0.045$.

‡ *Crystal data* for $[Ga{\cdot}\mathbf{1}].5H_2O$. $C_{27}H_{43}GaN_3O_{11}P_3$, $M = 748.3$, triclinic, space group $P\bar{1}$, $a = 11.883(3)$, $b = 12.468(4)$, $c = 11.842(5)$ Å, $\alpha = 99.39(3)$, $\beta = 98.47(3)$, $\gamma = 79.97(2)$°, $U = 1692(1)$ Å^3, $Z = 2$, $D_c = 1.469$ g cm^{-3}, $F(000) = 780$, μ(Mo-Kα) = 10.1 cm^{-1}; Intensity data were measured at 20 °C using an Enraf-Nonius CAD4 diffractometer. Lorentz, polarisation and absorption corrections were applied to the data; 7362 unique reflections were measured of which the 3149 with $I > 2.5\sigma(I)$ were used in the structural study. The structure was solved by the heavy atom method and refined by full-matrix least-squares calculations with the hydrogen atoms allowed for as riding atoms. At convergence $R = 0.051$, $R_w = 0.059$.

Atomic coordinates, bond lengths and angles, and thermal parameters for both structures have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

that the ligand adopts an almost identical conformation as in [Cu·**1**]$^-$. Again a single chiral diastereoisomer was formed although the neutral complex possessed only approximate C_3-symmetry. The complex is approximately octahedral with a twist angle of 7.9(4)° for the N_3 moiety relative to the O_3 which compares to 8.8(4)° for [Cu·**1**]$^-$. This was reflected in the ^{71}Ga NMR solution spectrum of [Ga·**1**] in which a rather broader singlet was observed [δ_{Ga}(pH − 0.7) = +132 ppm, $\omega_{1/2}$ = 560 Hz] compared to those found in [Ga·**2**] [δ_{Ga}(pH −0.7) = +136.3, $\omega_{1/2}$ = 212 Hz] or [Ga·NOTA][8] [δ_{Ga}(pH −0.7) = +171 ppm, $\omega_{1/2}$ = 210 Hz] both of which are C_3-symmetric in solution and kinetically stable with respect to dissociation in 6 mol dm^{-3} HNO_3. The neutral complex [Ga·**1**] dissolves readily in lower alcohols and is sparingly soluble in dichloromethane and chloroform; the more hydrophilic complex [Ga·**2**] is insoluble in these organic solvents and very soluble in water. ^{31}P Solution NMR analysis of the racemic mixture of [Ga·**1**] in [C_6D_6]benzene in the presence of the enantiopure chiral solvating agent (*S*)-2,2,2-trifluoro-1-(9-anthryl)ethanol revealed two equally intense singlets ($\Delta\delta_P$ = 0.19 ppm, 293 K) for the diastereoisomeric complexes. Resolution of the two complex enantiomers was also possible using a chiral HPLC column [Daicel, Chiralpak OT(+), Δt_R = 3 min, 5 °C MeOH] suggesting that such methods will afford preparative resolutions of the complex, as well as permitting precise enantiomeric purity determination.

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References

1 C. J. Broan, K. J. Jankowski, R. Kataky and D. Parker, *J. Chem. Soc., Chem. Commun.*, 1990, 1738.

2 C. J. Broan, K. J. Jankowski, R. Kataky, D. Parker, A. M. Randall and A. Harrison, *J. Chem. Soc., Chem. Commun.*, 1990, 1739; 1991, 204.

3 Examples of CuN_6, $Cu(N–N)_3$, CuO_6 or $Cu(O–O)_3$ chromophores that apparently exhibit an E_1 ground state at room temperature are rare but have been reported previously. Although apparently contradicting the Jahn–Teller theorem, which probhits orbitally degenerate ground states, the observed symmetry results from time-averaged distortions arising from electronic–vibronic coupling. These 'dynamic' distortions may be frozen out at lower temperatures *e.g.* $[Cu(en)_3]^{2+}$, D. L. Cullen and E. C. Lingafelter, *Inorg. Chem.*, 1970, **9**, 1858; I. Bertini, P. Dapporto, D. Gatteschi and A. Scozzafava, *J. Chem. Soc., Dalton Trans.*, 1979, 1409; $K_2PbCu(NO_2)_6$, D. L. Cullen and E. C. Lingafelter, *Inorg. Chem.*, 1971, **10**, 1264; B. Hathaway, J. Mullane, M. Duggan, A. Murphy, C. Power and B. Walsh, *Coord. Chem. Rev.*, 1981, **36**, 267. The so-called dynamic Jahn–Teller distortion has also been observed with bis(tribenzo[*b,f,j*][1,5,9]triazacyclododecine)copper(II), R. I. Sheldon, A. J. Jircitano, M. A. Beno, J. M. Williams and K. B. Mertes, *J. Am. Chem. Soc.*, 1983, **105**, 3028.

4 K. Wieghardt, U. Bossek, P. Chaudhuri, W. Herrmann, B. C. Menke and J. Weiss, *Inorg. Chem.*, 1982, **21**, 4308.

5 A. Bevilacqua, R. I. Gelb, W. B. Hebard and L. J. Zompa, *Inorg. Chem.*, 1987, **26**, 2699.

6 A. S. Craig, D. Parker, H. Adams and N. R. Bailey, *J. Chem. Soc., Chem. Commun.*, 1989, 1792. Observation of a ^{71}Ga (or ^{69}Ga) NMR signal in aqueous solution is restricted to complexes of high symmetry. Otherwise quadrupolar line broadening occurs through interaction of the electric field gradient at the gallium nucleus with the large quadrupole moment (0.112 for ^{71}Ga).