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Preparation and Structure of μ-(2,2′-Dipyridylamido-N^{α},N:N′)-μ-(2″,2‴-dipyridylamido-$N^{\alpha\prime}$,N″:N‴)bis {bis(pentafluorophenyl)thallium(III)} Unexpected Formation of a Four Membered Chelate Ring

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The 2,2′-dipyridylamide ion (dpa) normally chelates through the two pyridine nitrogen atoms giving a six-membered $\overline{\text{MNCNCN}}$ ring, [1, 2] and the amide nitrogen either is not coordinated as in $Pd(dpa)_2$ [1] or bridges to other metal atoms as in $\{Ni(dpa)_2\}_n$ or $\{Ni(dpa)_2\}_2NiCl_2$ [2]. 2,2′-Dipyridylamine chelates in the same way, and the amine nitrogen is not coordinated [3]. We now report the preparation and crystal structure of $\{(C_6F_5)_2Tl(dpa)\}_2 \cdot C_6H_6$, which, unexpectedly, has four membered $\underline{\text{TlNCN}}$ chelate rings.

Preparation and Characterization

Ready deprotonation of 2,2′-dipyridylamine occurred on reaction with an equimolar amount of $(C_6F_5)_3Tl(diox)$ [4] (diox=1,4-dioxan) in dry benzene at room temperature, and yellow crystals of $\{(C_6F_5)_2Tl(dpa)\}_2 \cdot C_6H_6$, m.p. 160–170 °C (slow dec. > 140 °C) were obtained on partial evaporation and addition of petroleum ether:

$$(C_6F_5)_3Tl(diox) + Hdpa \rightarrow (C_6F_5)_2Tl(dpa) + C_6F_5H + diox$$

A similar reaction was not observed for diphenylamine (only slightly less acidic than Hdpa [5]). The composition of the product was established by analysis, mass spectrometry {m/e corresponding to $(C_6F_5)_2Tl(dpa)^+$}, and PMR and infrared {no ν(NH)} spectroscopy. The electronic spectrum showed a maximum (358 nm) indicative [2] of deprotonated 2,2′-dipyridylamine. Molecular weight measurements in benzene were consistent with the equilibrium,

$$2\,(C_6F_5)_2Tl(dpa) \rightleftharpoons \{(C_6F_5)_2\,Tl(dpa)\}_2$$

suggesting an associated structure in the solid state.

Crystal Structure

The dimeric structure (Fig. 1) with bridging 2,2′-dipyridylamido ligands, novel four membered chelate rings, and benzene of crystallization, was established by X-ray crystallography. *Crystal Data*: $Tl_2C_{50}H_{22}N_6F_{20}$, M = 1495.5, triclinic, a = 16.641(5), b = 12.453(3), c = 12.035(5) Å, α = 92.89(2), β = 92.42(3), γ = 93.30(2)°; U = 2484 Å^3, D_m = 2.01(2) g cm^{-3}, Z = 2, D_c = 2.00 g cm^{-3}; Space group $P\bar{1}$, 2847 reflection intensities {Mo-K$_\alpha$; four circle diffractometer, graphite monochromator; $I \geqslant 3\sigma(I)$} formed the basis of the X-ray structural analysis (heavy atom method; full matrix least squares analysis of positional and anisotropic thermal parameters) which converged to ωR = 0.044.

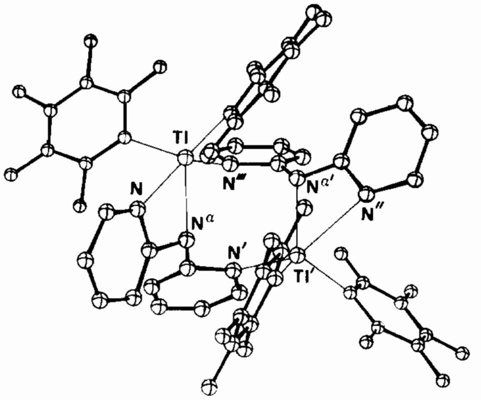

Fig. 1. Structure of title compound.

The dimer has no symmetry, but the dimensional differences between the two monomer units are generally within the error limits. Each thallium is five coordinate with very distorted (owing to the four membered ring) trigonal bipyramidal stereochemistry (Fig. 2), and is *ca.* 0.26Å out of the plane formed by the equatorial donor atoms. The equatorial thallium–ligand bonds {Tl–C(1), 2.16(4); Tl–C(1′), 2.12(4); Tl–N^{α}, 2.27(3) Å} are considerably shorter than the axial bonds {Tl–N, 2.57(4) Å; Tl–N‴, 2.46(3) Å}.

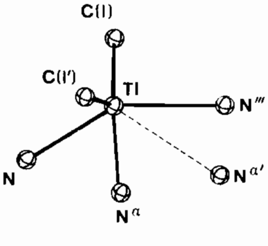

Fig. 2. Thallium co-ordination. C(1)–Tl–C(1′), 127(1)°; N–Tl–N^{α}, 56(1)°; N^{α}–Tl–C(1), 108(1)°; N–Tl–N‴ 144(1)°; N^{α}–Tl–C(1′), 122(1)°.

Similar stereochemistry is observed in polymeric $(C_6F_5)_2TlOH$ [6], and the thallium–pyridine nitrogen distances are comparable with those {2.57(3) [7] and 2.37(1) [8]} in 1,10-phenanthroline complexes of thallium(III). Although the Tl–$N^{\alpha\prime}$ and Tl′–N^{α} distances {3.32(3) and 3.18(3) Å respectively} are within the sum of the Van der Waals radii of thallium (1.96 Å [9]) and nitrogen, any interaction must be exceedingly weak, since the lone pair on each nitrogen is not directed towards the appropriate thallium and the distances are outside the sum of the covalent radius of thallium(III) (1.45–1.55 Å [10]) and the Van der Waals radius of nitrogen. There is probably only slight delocalisation of the negative charge on the amido nitrogen over the whole ligand {*cf.* (dpa) Ni(II) complexes [2]}, since this atom is much closer to thallium than the pyridine nitrogens. The ready dissociation of the dimer in the gas phase and in benzene can be attributed to the relatively weak bonding between the bridging pyridine nitrogen and thallium.

The mode of bonding of the 2,2′-dipyridylamido ligands and in particular the formation of the four membered rings may be attributed to the strong thallium–amido nitrogen interaction and the preferred trigonal arrangement of the three short thallium-ligand bonds {see also $(C_6F_5)_2TlOH$ [6]}. Since the two pyridyl rings cannot chelate to thallium giving a six-membered $\overline{\text{TlNCNCN}}$ ring without destroying the trigonal $TlC(1)C(1')N^{\alpha}$ arrangement, a four-membered $\underline{\text{TlNCN}}$ ring is formed leaving a second pyridine nitrogen available for bridging. Similar constraints do not apply in previously prepared 2,2′-dipyridylamido complexes [1, 2].

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