

Characterization of $[\text{Pb}(\text{NO}_3)(\text{ntam})_2]\text{NO}_3$, the First Metal Complex of the Neutral Tetradentate Ligand Nitrilotriacetamide (ntam)

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The first isolable, crystalline complex of nitrilotriacetamide with a metal and the first example of both a completely acyclic ligand and a 2 : 1 ligand : metal ratio in a ten-coordinate lead complex is reported.

It has been pointed out that the presence of neutral oxygen donors in a ligand can be used to control metal ion selectivity based on ion size.¹ Oxygen donors are not sufficient to ensure selectivity for Pb^{II} over smaller metal ions such as Zn^{II} ; the stereochemical activity of the lone electron pair of the Pb^{II} must be controlled.² According to valence shell electron pair repulsion (VSEPR) models, when this electron pair resides in a hybrid sp^n or $sp^m d^n$ orbital it is stereochemically active, and occupies a coordination site on the Pb^{II} . The coordination numbers for stereochemically active complexes tend to be 7 or less, and these complexes exhibit Pb–N bond lengths between 2.37 and 2.56 Å. The inactive lone pair is constrained to reside in a 6s (inner core) orbital by the stronger ligand field of more electron-rich ligands. Stereochemically inactive complexes have longer Pb–N bond lengths, between 2.62 and 2.88 Å.²

As part of our research efforts aimed at the synthesis and development of metal-selective complexing agents, we have been studying nitrilotriacetamide (ntam), **1**.³ Although both nitrilotriacetic acid **2** and the amide functional group are ubiquitous ligands for metal coordination, metal complexes of **1** have not been reported in the literature.^{4,5} We were particularly interested in whether **1** would bind to lead⁶ and, if so, with what stoichiometry, since the 1 : 1 complex could be seven-coordinate or less (stereochemically active) while the 2 : 1 complex would be at least eight-coordinate and presumably stereochemically inactive. We report here the first isolable, crystalline complex of **1** with a metal, lead, in a 2 : 1 stoichiometry.[†]

† A pale-yellow columnar crystal, $0.24 \times 0.50 \times 0.17$ mm, of nitrilotriacetamidelead nitrate was mounted on a glass fibre. Data were collected on an Enraf-Nonius CAD4 diffractometer with graphite monochromated Mo-K α radiation, using the ω -2 θ scan technique to a maximum of $2\theta = 52.0^\circ$. There were 4762 unique reflections from a total of 5113 collected. The structure was solved by Patterson and Fourier methods and refined by a full-matrix least-squares method (hydrogens as riding atoms), to an R value of 0.029. $\text{C}_{12}\text{H}_{28}\text{N}_{10}\text{O}_{14}\text{Pb}$; $M_r = 743.61$; triclinic, $P1$; $a = 8.457(1)$, $b = 11.549(2)$, $c = 13.228(2)$ Å, $\alpha = 79.40(1)$, $\beta = 73.12(1)$, $\gamma = 83.98^\circ(1)$; $V = 1213$ Å³, $Z = 2$; $D_c = 2.04$ g cm⁻³. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

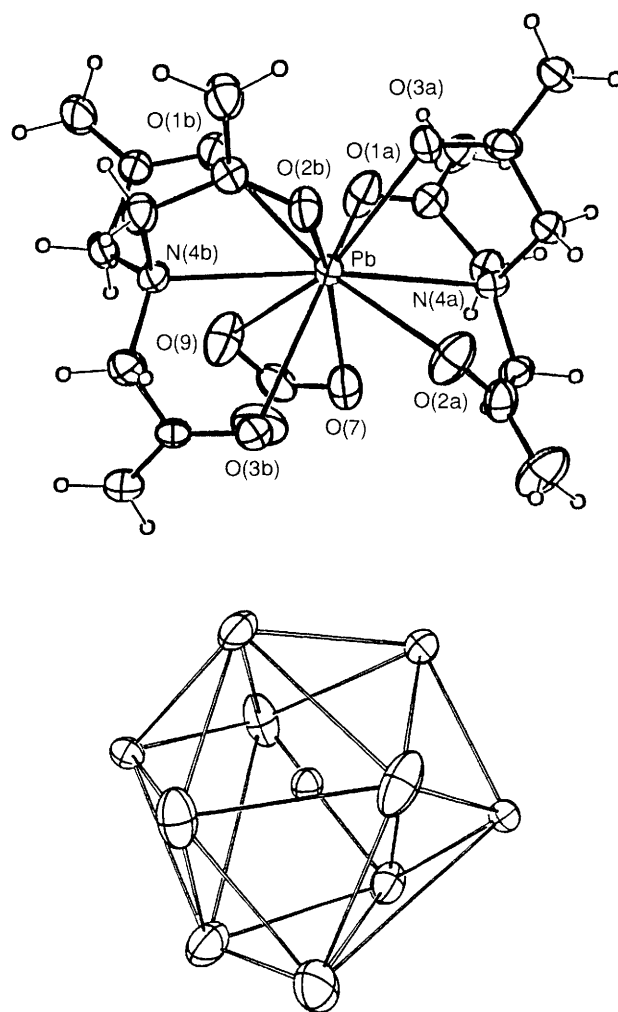
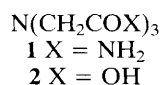


Fig. 1 (a) ORTEP plot and (b) coordination sphere of $[\text{Pb}(\text{NO}_3)(\text{ntam})_2]^+$. Thermal ellipsoids represent 50% probability.



Crystals of the 2:1 complex were obtained by slow evaporation from a 1:1 aqueous solution of **1** and $\text{Pb}(\text{NO}_3)_2$. No evidence for the formation of a 1:1 complex was observed. The structure of the 2:1 complex is shown in Fig. 1.

The lone electron pair on Pb in this structure is stereochemically inactive by all criteria. The lead is ten-coordinate, with Pb–N bond distances of 2.775 and 2.935 Å.⁷ This latter value is the longest reported Pb–N bond in a complex with a stereochemically inactive lone pair. The single nitrate ion binds to the lead in a bidentate fashion. Four of the six Pb–O distances average 2.668 ± 0.027 Å. The fifth oxygen lies 2.516 Å from the lead, while the remaining oxygen (which is in the same ntam ligand as the nitrogen that forms the long Pb–N bond, and forms an O–Pb–O angle of 154.0° with the oxygen in the other ntam ligand which makes the short Pb–O bond) is 2.825 Å from the lead. The long Pb–O and Pb–N distances are presumably due to the proximity of the bound nitrate (Fig. 1).

Ten-coordinate lead complexes are rare; this is the fourth one characterized and reported.⁷ Two of the previous complexes involved macrocyclic ligands,^{7a,c} the third a substituted 1,10-phenanthroline.^{7b} In these cases the single organic ligand provided six or eight bonds to the metal. $[\text{Pb}(\text{NO}_3)_2(\text{ntam})_2]\text{NO}_3$ represents the first example of both a completely acyclic ligand and a 2:1 ligand:metal ratio in a ten-coordinate lead complex.

These features, along with the high oxygen to nitrogen ratio, should provide high selectivity for lead over other, smaller metal ions. Studies with nitrilotriacetamide and derivatives of this ligand with Pb and other metals are in progress.

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