

# 1,3,5-Triamino-1,3,5-trideoxy-*cis*-inositol, a New Ligand with a Remarkable Versatility for Metal Ions. 4. Preparation, Characterization, and X-ray Structure of the Trinuclear Lead(II) and Bismuth(III) Complexes

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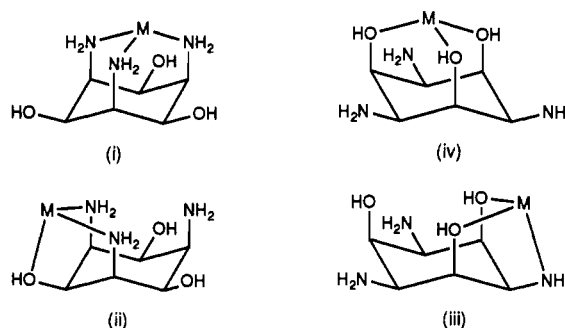
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Three compounds, containing the complexes  $[\text{Pb}_3(\text{H}_3\text{taci})]^{3+}$  and  $[\text{Bi}_3(\text{H}_3\text{taci})_2]^{3+}$  ( $\text{taci} = 1,3,5\text{-triamino-1,3,5-trideoxy-}i\text{-cis-inositol}$ ), have been prepared by combining solutions of  $\text{taci}$  and the corresponding metal nitrates. Single-crystal X-ray analysis of  $\text{Pb}_6(\text{H}_3\text{taci})_2(\text{NO}_3)_5(\text{OH})(\text{H}_2\text{O})_2$ ,  $P\bar{1}$ ,  $Z = 2$ ,  $a = 11.115(2)$  Å,  $b = 11.538(3)$  Å,  $c = 14.182(3)$  Å,  $\alpha = 107.75(2)^\circ$ ,  $\beta = 91.26(2)^\circ$ ,  $\gamma = 104.23(2)^\circ$ , and  $\text{Bi}_3(\text{H}_3\text{taci})_2\text{Cl}_3 \cdot 6\text{H}_2\text{O}$ ,  $R3$ ,  $Z = 3$ ,  $a = 8.114(1)$  Å,  $c = 35.960(7)$  Å, revealed the presence of trinuclear complexes, where each metal ion is bound to one terminal amino group and to two deprotonated, bridging hydroxyl groups of  $\text{taci}$ . The three metal ions and the three coordinated alkoxy groups of  $\text{taci}$  form a puckered, six-membered ring with a chair conformation. Rather short M–O and M–N bonds and small angles O–M–O and O–M–N were observed within the  $\text{M}_3(\text{H}_3\text{taci})$  fragments. In the case of the Pb complex, two  $[\text{Pb}_3(\text{H}_3\text{taci})]^{3+}$  entities were linked together by a nitrate ligand. All six Pb(II) atoms are coordinated to this bridging nitrate. The coordination number of Pb is 4. In the Bi(III) complex, two  $\text{taci}$  ligands surround the three metal ions in a sandwich type structure. Two additional Cl atoms are only weakly bound to Bi. The coordination number of Bi is  $6 + 2$ . The complexes are stable in aqueous solution and were characterized by NMR spectroscopy and  $\text{FAB}^+$  mass spectrometry. NMR data ( $\text{D}_2\text{O}$ ) are in agreement with the highest possible symmetry  $\text{C}_{3v}$  for the Pb(II) complex and  $\text{D}_{3h}$  for the Bi(III) complex. In the  $\text{FAB}^+$  mass spectra (glycerol matrix), the most intense peaks were assigned to  $[\text{Pb}_3(\text{taci})(\text{glycerol}) - 5\text{H}]^+$  and  $[\text{Bi}_3(\text{taci})_2 - 8\text{H}]^+$ .

## Introduction

During a systematic investigation of metal complexes with 1,3,5-triamino-1,3,5-trideoxy-*cis*-inositol ( $\text{taci}$ ), a variety of bis complexes  $\text{M}(\text{taci})_2^{z+}$  ( $z = 2-4$ ) were prepared and studied in our laboratory.<sup>2-6</sup> Four distinct metal binding sites (Chart I), providing different  $\text{N}_x\text{O}_y$  environments ( $x + y = 3$ ), are responsible for the high versatility of this ligand. However, the various forms of coordination complicate the elucidation of the molecular structure: A total of 10 different isomers must be considered for a given complex  $\text{M}(\text{taci})_2^{z+}$ . Previous contributions reported the observation of 3 of the 10 possible structure types: bis type i ( $\text{M} = \text{Ni}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Co}^{3+}$ ,  $\text{Ti}^{3+}$ ),<sup>4-6</sup> bis type iv ( $\text{Al}^{3+}$ ,  $\text{Cr}^{3+}$ ),<sup>3,6</sup> and type i/type iv ( $\text{M} = \text{Cr}^{3+}$ ,  $\text{Ga}^{3+}$ ).<sup>3,6</sup> It is interesting to note that the binding of the metal to the "asymmetric" sites ii and iii has not been observed as yet. Due to the large ionic radii and the high affinity for either N or O donor atoms, Pb(II) and Bi(III) were promising candidates for the binding to these particular sites. Moreover, complexes of  $\text{taci}$  with these metals may be of interest either as precursors for new materials of technological value<sup>7,8</sup> or also with regard to an application in medicine.<sup>9</sup> The investigation of the Pb(II) and Bi(III) complexes of  $\text{taci}$  has

## Chart I<sup>a</sup>



<sup>a</sup> The coordinated oxygen atoms in these schematic representations are shown as remaining protonated although this is not the case in their complexes with trivalent metal cations.

therefore been included in our research work. In the present contribution, we report the preparation, characterization, and X-ray structure of two novel trinuclear Pb(II) and Bi(III) complexes.

## Experimental Section

**Spectroscopy, Mass Spectrometry, and Analyses.**  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were measured on a Bruker AC-200 spectrometer with  $\delta$  (ppm) scale and sodium (trimethylsilyl)propionate- $d_4$  ( $=0$  ppm) as internal standard. The  $\text{FAB}^+$ -MS spectra were run on a VG ZAB VSEQ instrument. Test solutions were prepared by dissolving the samples in water and mixing the resulting solutions with a glycerol matrix prior to the introduction in the spectrometer. IR spectra were recorded on a Perkin-Elmer 883 infrared spectrophotometer; data are given in  $\text{cm}^{-1}$ . C,H,N analyses were performed by D. Manser, Laboratorium für Organische Chemie, ETH Zürich, Switzerland.

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- (1) (a) Laboratorium für Anorganische Chemie. (b) Institut für Kristallographie und Petrographie.
- (2) Hegetschweiler, K.; Erni, I.; Schneider, W.; Schmalte, H. *Helv. Chim. Acta* **1990**, *73*, 97.
- (3) Schmalte, H. W.; Hegetschweiler, K.; Ghisletta, M. *Acta Crystallogr.* **1991**, *C47*, 2047.
- (4) Hegetschweiler, K.; Gramlich, V.; Ghisletta, M.; Samaras, H. *Inorg. Chem.* **1992**, *31*, 2341.
- (5) Ghisletta, M.; Jalett, H.-P.; Gerfin, T.; Gramlich, V.; Hegetschweiler, K. *Helv. Chim. Acta* **1992**, *75*, 2233.
- (6) Hegetschweiler, K.; Ghisletta, M.; Fässler, T. F.; Nesper, R.; Schmalte, H. W.; Rihs, G. *Inorg. Chem.* **1993**, *32*, 2032.
- (7) Papiernik, R.; Hubert-Pfalzgraf, L. G.; Massiani, M. C. *Polyhedron* **1991**, *10*, 1657 and references therein.
- (8) (a) Massiani, M.-C.; Papiernik, R.; Hubert-Pfalzgraf, L. G.; Daran, J.-C. *Polyhedron* **1991**, *10*, 437. (b) Massiani, M.-C.; Papiernik, R.; Hubert-Pfalzgraf, L. G.; Daran, J.-C. *J. Chem. Soc., Chem. Commun.* **1990**, 301.

- (9) (a) Peterson, W. L. *J. Clin. Gastroenterol.* **1990**, *12* (Suppl. 2), S1. (b) Slomiany, B. L.; Nishikawa, H.; Bilski, J.; Slomiany, A. *Am. J. Gastroenterol.* **1990**, *85*, 390. (c) Bianchi Porro, G.; Parente, F. *J. Clin. Gastroenterol.* **1992**, *14*, 192.

**Table I.** Crystallographic Data for  $[\text{Pb}_6(\text{H}_3\text{taci})_2(\text{NO}_3)](\text{NO}_3)_4(\text{OH})\cdot 2\text{H}_2\text{O}$  and  $[\text{Bi}_3(\text{H}_3\text{taci})_2]\text{Cl}_3\cdot 6\text{H}_2\text{O}$ 

	Pb complex	Bi complex
formula	$\text{C}_{12}\text{H}_{29}\text{N}_{11}\text{O}_{24}\text{Pb}_6$	$\text{C}_{12}\text{H}_{16}\text{Bi}_3\text{Cl}_3\text{N}_6\text{O}_{12}$
fw	1954.6	1189.8
cryst size, mm	$0.1 \times 0.2 \times 0.25$	$0.2 \times 0.2 \times 0.07$
space group	$\bar{P}1$ (No. 2)	$R\bar{3}$ (No. 146)
crystal system	triclinic	trigonal
<i>a</i> , Å	11.115(2)	8.114(1)
<i>b</i> , Å	11.538(3)	8.114(1)
<i>c</i> , Å	14.182(3)	35.960(7)
$\alpha$ , deg	107.75(2)	90.0
$\beta$ , deg	91.26(2)	90.0
$\gamma$ , deg	104.23(2)	120.0
<i>V</i> , Å <sup>3</sup>	1669.8(6)	2050.3(5)
<i>Z</i>	2	3
<i>T</i> , °C	17	17
$\lambda(\text{Mo K}\alpha)$ , Å	0.71073	0.71073
$\rho_{\text{calcd}}$ , g/cm <sup>3</sup>	3.89	2.89
$\mu$ , cm <sup>-1</sup>	304.8	195.7
transm. coeff	0.0148/0.0896	0.3587/0.6337
<i>R</i> ( <i>F</i> <sub>o</sub> ), %	4.4	3.8
<i>R</i> <sub>w</sub> ( <i>F</i> <sub>o</sub> ), %	4.3	3.8

$a R = \sum |F_o| - |F_c| / \sum |F_o|$ ;  $b R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}$ ;  $w = 1/\sigma^2(|F_o|)$ .

**Preparation of the Complexes.** Taci was prepared as described in ref 5.  $\text{Bi}(\text{NO}_3)_3\cdot 5\text{H}_2\text{O}$ ,  $\text{Pb}(\text{NO}_3)_2$ , MeOH, and  $\text{N}(\text{Et}_3)$ , commercially available compounds of reagent grade quality, were used without further purification.

(1)  $[\text{Pb}_6(\text{H}_3\text{taci})_2(\text{NO}_3)](\text{NO}_3)_4(\text{OH})\cdot 2\text{H}_2\text{O}$ . (a) An aqueous solution of  $\text{Pb}(\text{NO}_3)_2$  (0.45 g, 1.37 mmol) in 3 mL of  $\text{H}_2\text{O}$  was added to an aqueous solution of taci (0.49 g, 2.77 mmol) in 3 mL of  $\text{H}_2\text{O}$ . The precipitated white solid was redissolved by heating, and the solution was allowed to stand for 12 h at room temperature. Yield: 0.38 g (86%) of colorless crystals. (b)  $\text{Pb}(\text{NO}_3)_2$  [2.0 g (6 mmol)], taci [0.36 g (2 mmol)], and  $\text{N}(\text{Et}_3)$  [0.72 g (7.2 mmol)] were added to 60 mL of water. The suspension was refluxed for 1 h, filtered hot, and allowed to stand at 4 °C for 2 days. Yield: 1.44 g (73%) of colorless crystals. Anal. Calcd for  $\text{C}_{12}\text{H}_{29}\text{N}_{11}\text{O}_{22}\text{Pb}_6\cdot 2\text{H}_2\text{O}$ : C, 7.37; H, 1.50; N, 7.88. Found: C, 7.37; H, 1.24; N, 7.56. IR (KBr): 3405, 3242, 3141, 2883, 1592, 1430 (sh), 1405 (sh), 1383, 1375 (sh), 1350, 1320 (sh), 1275 (sh), 1123, 1012, 930, 870, 850, 811, 792, 772, 605, 504, 480, 346. <sup>13</sup>C NMR ( $\text{D}_2\text{O}$ ): 75.8, 62.4.

(2)  $[\text{Bi}_3(\text{H}_3\text{taci})_2](\text{NO}_3)_3\cdot 0.5\text{CH}_3\text{OH}$ . Taci [0.33 g (1.9 mmol)] was dissolved in 20 mL of  $\text{CH}_3\text{OH}$ ; 0.59 g (5.8 mmol) of  $\text{N}(\text{Et}_3)$  and 1.35 g (2.8 mmol) of  $\text{Bi}(\text{NO}_3)_3\cdot 5\text{H}_2\text{O}$  were then added. The suspension was refluxed for 3 h and allowed to stand at room temperature for additional 12 h. A white solid was filtered off and dried in vacuo over  $\text{P}_2\text{O}_5$ . Yield: 1.06 g (97%). Anal. Calcd for  $\text{C}_{12}\text{H}_{24}\text{N}_9\text{O}_{15}\text{Bi}_3\cdot 0.5\text{CH}_3\text{OH}$ : C, 12.75; H, 2.23; N, 10.71. Found: C, 12.67; H, 2.25; N, 10.64. IR (KBr): 3430, 3249, 3156, 2870, 2840, 2424, 1762, 1594, 1377, 1320 (sh), 1265, 1217, 1126, 1093, 1051, 978, 953 (sh), 926, 875, 823, 778, 525, 481, 367. <sup>1</sup>H NMR: see Figure 7d, additional singlet at 3.38 ppm (MeOH).

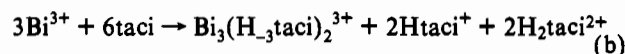
(3)  $[\text{Bi}_3(\text{H}_3\text{taci})_2]\text{Cl}_3\cdot 4\text{H}_2\text{O}$  was obtained from  $[\text{Bi}_3(\text{H}_3\text{taci})_2](\text{NO}_3)_3\cdot 0.5\text{CH}_3\text{OH}$  by ion-exchange (Dowex 1, Cl<sup>-</sup> form) and recrystallized from  $\text{H}_2\text{O}$ . Yield: 65%. Anal. Calcd for  $\text{C}_{12}\text{H}_{24}\text{N}_6\text{O}_6\text{Bi}_3\cdot 4\text{H}_2\text{O}$ : C, 12.49; H, 2.80; N, 7.28. Found: C, 12.50; H, 2.83; N, 7.23. IR (KBr): 3383, 3328, 3262, 3154, 2871, 2851, 2811, 1647, 1599, 1383, 1347, 1265, 1219, 1127, 1098, 1049, 1014, 975, 953, 927, 875, 795, 781, 635, 606, 523, 482, 370. <sup>13</sup>C NMR ( $\text{D}_2\text{O}$ ): 80.2, 60.5. Single crystals of the composition  $[\text{Bi}_3(\text{H}_3\text{taci})_2]\text{Cl}_3\cdot 6\text{H}_2\text{O}$ , suitable for X-ray analysis, were grown by slow evaporation of water from a saturated aqueous solution of the product at room temperature.

**X-ray Diffraction Studies.** Data collection was performed with a SYNTEX-P21 four-circle diffractometer. Crystallographic data are summarized in Table I. A standard reflection was measured at an interval of every 120 reflections; no loss of intensities was noted. The data were corrected for Lorentz and polarization effects, and a face-indexed numerical absorption correction was applied. The structures were solved by direct methods using Siemens SHELXTL-PLUS (VMS)<sup>10</sup> and refined by full-matrix least-squares calculations using anisotropic displacement parameters for all non-hydrogen atoms except the C atoms of the Bi complex, which were refined isotropically. Four Cl positions were localized

during the structure determination of the Bi complex; however, the molecular formula requires only 3 Cl<sup>-</sup> ions. Accordingly, the calculations were performed with occupancy factors of 0.75 for these four positions. It is, however, highly probable that 3 chlorine atoms and 1 water molecule occupy these positions at random, with a slight preference of chlorine for positions 1 and 4 as indicated by the lower *U*<sub>eq</sub> values. The atomic coordinates are shown in Table II. A summary of bond distances and bond angles is presented in Tables III and IV.

## Results and Discussion

**Preparation of the Complexes.** We actually intended to prepare  $\text{Pb}(\text{taci})_2^{2+}$  and  $\text{Bi}(\text{taci})_2^{3+}$  according to the methods used previously for a variety of other divalent and trivalent metal ions.<sup>4,6</sup> Therefore, solutions containing the metal on the one hand and the free ligand on the other hand were combined in a 1:2 molar ratio. The combination of the two solutions resulted in the immediate precipitation of a white solid. However, analysis of these solids showed that, instead of the expected bis complexes, species with a much lower ligand to metal ratio were formed. The initial reactions in solution can be described by the equations



Obviously, a part of the taci used acted as base rather than as ligand and could be replaced by a less expensive reagent like  $\text{N}(\text{Et}_3)$ . In this way, the preparation could be readily performed with high yields using the appropriate stoichiometric quantities of the metal nitrates, taci, and  $\text{N}(\text{Et}_3)$ . The conversion of the nitrates to the corresponding chlorides was easily achieved by ion-exchange chromatography.

**Crystal Structure of  $[\text{Pb}_6(\text{H}_3\text{taci})_2(\text{NO}_3)](\text{NO}_3)_4(\text{OH})\cdot 2\text{H}_2\text{O}$ .** A view of the complex is given in Figure 1. Three Pb(II) atoms are bound to the three "asymmetric" sites iii (Chart I) of one taci molecule, forming two five-membered and one six-membered chelate ring per Pb(II). The six-membered chelate ring has a boat conformation. The three alkoxy groups of taci act as  $\mu_2$ -bridges whereas each of the three terminal amino groups is bound to one metal atom only. The three Pb atoms and the three O atoms form a puckered, six-membered ring with a chair conformation. There is no crystallographic symmetry of this rigid  $[\text{Pb}_3(\text{H}_3\text{taci})]^{3+}$  fragment; however, the deviation from  $C_{3v}$  is only small. Rather short Pb-O and Pb-N distances<sup>11</sup> and remarkably small angles O-Pb-O and O-Pb-N are observed within this fragment. The Pb-Pb distances are in the same range as found for several other polynuclear Pb(II) complexes.<sup>12</sup> Hancock et al. determined bond angles and bond lengths with minimum strain energy for five-membered and six-membered chelate rings by molecular mechanics calculations.<sup>13</sup> It is interesting to note that the observed O-Pb-N angles of 68–72° in the present Pb complex (Table IV) are in close agreement with the calculated optimum of 69° for a five-membered chelate ring. This is not the case for the O-Pb-O bond angles in the six-membered rings. The observed values of 79–83° are significantly smaller than the optimum of 109.5°.

- (11) Pb-O distances, reported in literature, cover the rather wide range from 2.2 to 3.0 Å; Pb-N distances range from 2.4 to 2.8 Å. See, e.g.: (a) Tandon, S. S.; McKee, V. *J. Chem. Soc., Dalton Trans.* **1989**, 19. (b) Adams, H.; Bailey, N. A.; Fenton, D. E.; Good, R. J.; Moody, R.; Rodriguez de Barbarin, C. O. *J. Chem. Soc., Dalton Trans.* **1987**, 207. (c) Drew, M. G. B.; Rodgers, A.; McCann, M.; Nelson, S. M. *J. Chem. Soc., Chem. Commun.* **1978**, 415. (d) Bailey, N. A.; Fenton, D. E.; Jackson, I. T.; Moody, R.; Rodriguez de Barbarin, C. *J. Chem. Soc., Chem. Commun.* **1983**, 1463. (e) Jovanovski, G.; Hergold-Brundic, A.; Kamenar, B. *Acta Crystallogr.* **1988**, C44, 63. (f) Hardin, S. G.; Healy, P. C.; Mumme, W. G.; White, A. H.; Winter, G. *Aust. J. Chem.* **1982**, 35, 2423. (g) Beveridge, K. A.; Bushnell, G. W. *Can. J. Chem.* **1979**, 57, 2498. (h) Tadokoro, M.; Sakiyama, H.; Matsumoto, N.; Okwa, H.; Kida, S. *Bull. Chem. Soc. Jpn.* **1990**, 63, 3337. See also refs 12, 14, 15, 23, 24, and 31.
- (12) (a) Spiro, T. G.; Templeton, D. H.; Zalkin, A. *Inorg. Chem.* **1969**, 8, 856. (b) Olin, Å.; Söderquist, R. *Acta Chem. Scand.* **1972**, 26, 3505. (c) Pierce-Butler, M. A. *Acta Crystallogr.* **1984**, C40, 1364.
- (13) Hancock, R. D. *Prog. Inorg. Chem.* **1989**, 37, 187.

(10) Sheldrick, G. M. *SHELXTL-PLUS 88. Structure Determination Software Programs*; Nicolet Instrument Corp.: Madison, WI, 1988.

**Table II.** Atomic Coordinates and Isotropic or Equivalent Isotropic Temperature Factors with Estimated Standard Deviations in Parenthesis for Non-Hydrogen Atoms of  $[\text{Pb}_6(\text{H}_3\text{taci})_2(\text{NO}_3)](\text{NO}_3)_4(\text{OH})\cdot 2\text{H}_2\text{O}$  and  $[\text{Bi}_3(\text{H}_3\text{taci})_2]\text{Cl}_3\cdot 6\text{H}_2\text{O}$

atom	x	y	z	$U_{\text{eq}}/U_{\text{iso}}, \text{\AA}^2$
Pb Complex				
Pb(11)	0.1079(1)	0.2468(1)	0.2310(1)	0.027(1)
Pb(12)	0.4544(1)	0.2441(1)	0.2128(1)	0.035(1)
Pb(13)	0.1938(1)	-0.0212(1)	0.0156(1)	0.032(1)
Pb(21)	0.3371(1)	-0.2233(1)	0.3026(1)	0.030(1)
Pb(22)	-0.0193(1)	-0.2550(1)	0.2603(1)	0.028(1)
Pb(23)	0.1969(1)	0.0231(1)	0.4880(1)	0.030(1)
C(11)	0.133(2)	0.233(2)	0.005(1)	0.032(7)
C(12)	0.179(2)	0.373(2)	0.069(1)	0.027(7)
C(13)	0.306(2)	0.411(2)	0.131(1)	0.028(7)
C(14)	0.402(2)	0.374(2)	0.062(1)	0.026(7)
C(15)	0.367(2)	0.237(2)	-0.006(1)	0.030(7)
C(16)	0.235(2)	0.204(2)	-0.064(1)	0.028(7)
O(11)	0.101(1)	0.151(1)	0.0623(7)	0.024(4)
O(13)	0.302(1)	0.354(1)	0.2103(8)	0.028(5)
O(15)	0.371(1)	0.149(1)	0.0463(8)	0.029(5)
N(12)	0.083(1)	0.399(1)	0.1413(9)	0.027(6)
N(14)	0.519(1)	0.394(1)	0.123(1)	0.034(6)
N(16)	0.198(2)	0.068(1)	-0.1192(9)	0.035(6)
C(21)	0.245(2)	-0.229(2)	0.516(1)	0.023(7)
C(22)	0.219(2)	-0.366(2)	0.447(1)	0.029(7)
C(23)	0.104(2)	-0.407(2)	0.372(1)	0.027(7)
C(24)	-0.012(2)	-0.377(2)	0.424(1)	0.029(7)
C(25)	0.011(2)	-0.239(2)	0.489(1)	0.026(7)
C(26)	0.128(2)	-0.204(2)	0.563(1)	0.025(7)
O(21)	0.293(1)	-0.141(1)	0.4652(8)	0.035(5)
O(23)	0.128(1)	-0.350(1)	0.2950(8)	0.029(5)
O(25)	0.023(1)	-0.156(1)	0.4310(8)	0.024(4)
N(22)	0.329(1)	-0.380(1)	0.390(1)	0.027(6)
N(24)	-0.115(1)	-0.409(1)	0.347(1)	0.026(5)
N(26)	0.151(1)	-0.070(1)	0.6186(9)	0.026(5)
N	0.154(2)	-0.002(2)	0.253(1)	0.043(7)
O(1N)	0.230(1)	0.075(1)	0.2175(9)	0.046(6)
O(2N)	0.188(1)	-0.077(1)	0.2858(9)	0.043(6)
O(3N)	0.035(1)	-0.003(1)	0.248(1)	0.044(6)
N(1)	-0.250(2)	0.240(1)	0.195(1)	0.035(7)
O(11N)	-0.335(1)	0.176(1)	0.1226(9)	0.047(6)
O(12N)	-0.274(1)	0.322(1)	0.265(1)	0.056(6)
O(13N)	-0.146(1)	0.217(2)	0.192(1)	0.060(8)
N(2)	0.630(2)	-0.235(1)	0.307(1)	0.037(7)
O(21N)	0.584(1)	-0.167(1)	0.3777(9)	0.038(5)
O(22N)	0.557(1)	-0.317(1)	0.237(1)	0.055(6)
O(23N)	0.742(1)	-0.215(1)	0.308(1)	0.048(6)
N(3)	0.364(2)	0.352(2)	0.480(2)	0.057(9)
O(31N)	0.452(2)	0.307(2)	0.441(1)	0.09(1)
O(32N)	0.377(2)	0.411(2)	0.569(1)	0.10(1)
O(33N)	0.267(2)	0.346(2)	0.430(1)	0.10(1)
N(4)	0.208(2)	-0.354(2)	0.017(2)	0.06(1)
O(41N)	0.316(1)	-0.330(2)	0.055(1)	0.058(7)
O(42N)	0.182(2)	-0.423(2)	-0.073(1)	0.077(9)
O(43N)	0.126(2)	-0.310(2)	0.057(2)	0.12(1)
O(1W)	0.467(1)	0.062(1)	0.4119(9)	0.055(6)
O(2W)	0.603(1)	0.003(1)	0.2499(9)	0.050(6)
O(3W)	0.431(2)	-0.072(2)	0.086(1)	0.071(8)
Bi Complex				
Bi	-0.2693(1)	0.0000(1)	0.0	0.027(1)
Cl(1) <sup>b</sup>	-0.3333	0.3333	0.0029(3)	0.032(3)
Cl(2) <sup>b</sup>	0.6667	0.3333	0.1381(4)	0.046(3)
Cl(3) <sup>b</sup>	0.0	0.0	0.2007(3)	0.048(3)
Cl(4) <sup>b</sup>	-0.6667	-0.3333	0.0041(3)	0.034(3)
O(1)	-0.004(2)	0.200(2)	0.0370(3)	0.026(4)
O(2)	-0.205(2)	-0.208(2)	-0.0321(3)	0.029(5)
N(1)	-0.351(2)	-0.002(3)	0.0731(3)	0.023(6)
N(2)	-0.347(3)	-0.002(2)	-0.0654(6)	0.041(7)
C(1)	-0.177(3)	-0.002(3)	0.0897(5)	0.032(4)
C(2)	0.000(2)	0.183(2)	0.0758(4)	0.019(3)
C(3)	-0.180(2)	-0.002(2)	-0.0844(4)	0.019(3)
C(4)	-0.180(3)	-0.178(3)	-0.0713(6)	0.040(4)
O(1W)	0.3333	0.6667	0.212(1)	0.058(9)
O(2W)	0.3333	0.6667	0.126(1)	0.07(1)
O(3W)	0.031(3)	0.365(4)	0.1695(7)	0.09(1)

<sup>a</sup>  $U_{\text{eq}} = 1/3 \sum_i \sum_j U_{ij} a_i^* a_j^* a_i a_j$ . <sup>b</sup> A population parameter of 0.75 was used for these positions; see text.

Two  $[\text{Pb}_3(\text{H}_3\text{taci})]^{3+}$  fragments are linked together by a bridging nitrate. The binding of six Pb(II) atoms to one single nitrate is unusual. However, the Pb-O<sub>NO</sub> bond lengths are not

abnormal.<sup>14</sup> The distances to further ligands (NO<sub>3</sub><sup>-</sup>, OH<sup>-</sup>) are very long,<sup>15</sup> indicating only weak ionic interactions. Thus, the first coordination sphere of each Pb is restricted to the three donor atoms of taci, and the bridging nitrate (coordination number of Pb = 4) and can be described as a distorted square pyramid with a lone pair in the apex.

**Crystal Structure of  $[\text{Bi}_3(\text{H}_3\text{taci})_2]\text{Cl}_3\cdot 6\text{H}_2\text{O}$ .** The structure of the trinuclear Bi(III) complex is closely related to the above-described Pb(II) complex (Figure 2). Again, three Bi atoms are bound tightly<sup>16</sup> to the three "asymmetric" sites iii (Chart I) of one taci molecule. In contrast to the Pb complex, where the bridging nitrate ligand completed the coordination sphere, the  $\text{Bi}_3(\text{H}_3\text{taci})$  fragment is coordinated to an additional  $\text{H}_3\text{taci}^{3-}$  entity, forming a kind of sandwich structure. The idealized symmetry of the entire  $[\text{Bi}_3(\text{H}_3\text{taci})_2]^{3+}$  complex is  $D_{3h}$ . However, due to the rhombohedral packing, the crystallographic symmetry is only  $C_3$ . The deviation from  $C_{3v}$  is low, but deviation from  $D_{3h}$  is significant, expressed by distinctly different distances between Bi and the two axial nitrogen atoms. The coordination sphere of Bi can be described as a 6 + 2 environment with two long Bi-Cl distances. Each of the two atoms Cl(1) and Cl(4) is bridging 2 Bi atoms of two different  $[\text{Bi}_3(\text{H}_3\text{taci})_2]$  cores. Cl(2) and Cl(3) do not interact with the Bi atoms at all.

**Spectroscopic Characterization.** IR spectroscopy has repeatedly been used to characterize nitrate complexes.<sup>17,18</sup> In particular, the N-O stretching mode  $\nu_3$  (1380 cm<sup>-1</sup> for ionic nitrate) and the combination mode  $\nu_1 + \nu_4$  (1700-1800 cm<sup>-1</sup>) have been used to characterize the binding of NO<sub>3</sub><sup>-</sup> to a metal ion. The IR spectra of the nitrate-containing taci Pb(II) and Bi(III) complexes exhibited a sharp band at 1760 cm<sup>-1</sup> and a strong, broad, and poorly resolved band at 1450-1300 cm<sup>-1</sup> with a maximum at 1380 cm<sup>-1</sup> and various shoulders. These values indicate the presence of a considerable amount of ionic nitrate. However, as already pointed out elsewhere,<sup>18</sup> the IR data alone do not allow an unambiguous characterization of the coordination type of nitrate.

FAB mass spectrometry proved to be a valuable tool to infer the binding of the metal to taci on one hand and to the peripheral ligands (Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup>) on the other. As already recognized previously, the observed species distribution basically reflects solution chemistry in the matrix.<sup>4,6,19</sup> A variety of metal-containing peaks were assigned in the spectrum of the three compounds (Figures 3-6, Table V), and several species containing the trinuclear fragments  $[\text{Pb}_3(\text{taci}) - x\text{H}]$  and  $[\text{Bi}_3(\text{taci})_2 - y\text{H}]$  were observed. The monocationic charge of these species was obtained by multiple deprotonation. Since the hydroxyl groups

- (14) (a) Bashall, A.; McPartlin, M.; Murphy, B. P.; Fenton, D. E.; Kitchen, S. J.; Tasker, P. A. *J. Chem. Soc., Dalton Trans.* 1990, 505. (b) Aghabozorg, H.; Palenik, R. C.; Palenik, G. J. *Inorg. Chim. Acta* 1986, 111, L53. (c) Engelhardt, L. M.; Patrick, J. M.; White, A. H. *Aust. J. Chem.* 1989, 42, 335.
- (15) Koziol, A. E.; Palenik, R. C.; Palenik, G. J. *Inorg. Chim. Acta* 1986, 116, L51.
- (16) Reported Bi-O distances range from 2.1 to 3.0 Å, Bi-N distances from 2.4 to 2.9 Å; see: (a) Belicchi Ferrari, M.; Calzolari Capacchi, L.; Cavalca, L.; Fava Gasparri, G. *Acta Crystallogr.* 1972, B28, 1169. (b) Bensch, W.; Blazso, E.; Dubler, E.; Oswald, H. R. *Acta Crystallogr.* 1987, C43, 1699. (c) Evans, W. J.; Hain, J. H.; Ziller, J. W. *J. Chem. Soc., Chem. Commun.* 1989, 1628. (d) Alcock, N. W.; Ravindran, M.; Willey, G. R. *J. Chem. Soc., Chem. Commun.* 1989, 1063. (e) Battaglia, L. P.; Bonamartini Corradi, A.; Pelizzi, C.; Pelosi, G.; Tarasconi, P. *J. Chem. Soc., Dalton Trans.* 1990, 3857 and references therein. (f) Battaglia, L. P.; Bonamartini Corradi, A.; Pelosi, G.; Tarasconi, P.; Pelizzi, C. *J. Chem. Soc., Dalton Trans.* 1989, 671. (g) Suyarov, K. D.; Shkol'nikova, L. M.; Porai-Koshits, M. A.; Fundamenskii, V. S.; Davidovich, R. L. *Dokl. Chem. (Engl. Transl.)* 1990, 310, 93. (h) Shchelokov, R. N.; Mikhailov, Yu. N.; Mistryukov, V. E.; Sergeev, A. V. *Dokl. Chem. (Engl. Transl.)* 1987, 294, 162. See also refs 26, 28, and 30.
- (17) Lever, A. B. P.; Mantovani, E.; Ramaswamy, B. S. *Can. J. Chem.* 1971, 49, 1957.
- (18) Kleywegt, G. J.; Wiesmeijer, W. G. R.; Van Driel, G. J.; Driessen, W. L.; Reedijk, J.; Noordik, J. H. *J. Chem. Soc., Dalton Trans.* 1985, 2177.
- (19) Hegetschweiler, K.; Caravatti, P.; Fedin, V. P.; Sokolov, M. N. *Helv. Chim. Acta* 1992, 75, 1659.

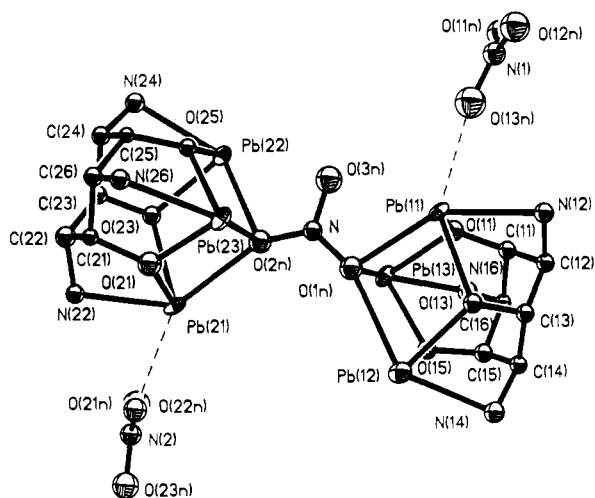
**Table III.** Summarized Interatomic Distances (Å) of  $[\text{Pb}_6(\text{H}_3\text{taci})_2(\text{NO}_3)](\text{NO}_3)_4(\text{OH})\cdot 2\text{H}_2\text{O}$  and  $[\text{Bi}_3(\text{H}_3\text{taci})_2]\text{Cl}_3\cdot 6\text{H}_2\text{O}$ , with Estimated Standard Deviations in Parentheses

bond	$[\text{Pb}_6(\text{H}_3\text{taci})_2(\text{NO}_3)](\text{NO}_3)_4(\text{OH})\cdot 2\text{H}_2\text{O}$		$[\text{Bi}_3(\text{H}_3\text{taci})_2]\text{Cl}_3\cdot 6\text{H}_2\text{O}$	
	av	range	av	range
M–N	2.46	2.42(2)–2.52(2)	2.57	2.43(2)–2.71(1)
M–O	2.34	2.29(1)–2.40(1)	2.33	2.28(2)–2.40(1)
C–C	1.54	1.52(2)–1.57(3)	1.54	1.50(3)–1.55(2)
C–N	1.48	1.46(2)–1.52(2)	1.52	1.52(3)–1.53(3)
C–O	1.44	1.42(2)–1.45(2)	1.42	1.40(2)–1.43(2)
M–Cl			3.00	3.000(3)–3.002(3)
M–ONO <sub>3</sub> ,bridg	2.69	2.62(1)–2.78(2)		
M–ONO <sub>3</sub> ,term	2.91	2.77(2)–3.05(2)		
M–OH	3.04			
M...M	3.932	3.873(2)–4.006(2)	3.784(1)	

**Table IV.** Summarized Bond Angles (deg) of  $[\text{Pb}_6(\text{H}_3\text{taci})_2(\text{NO}_3)]^{5+}$  and  $[\text{Bi}_3(\text{H}_3\text{taci})_2]\text{Cl}_3$ , with Estimated Standard Deviations in Parentheses<sup>a</sup>

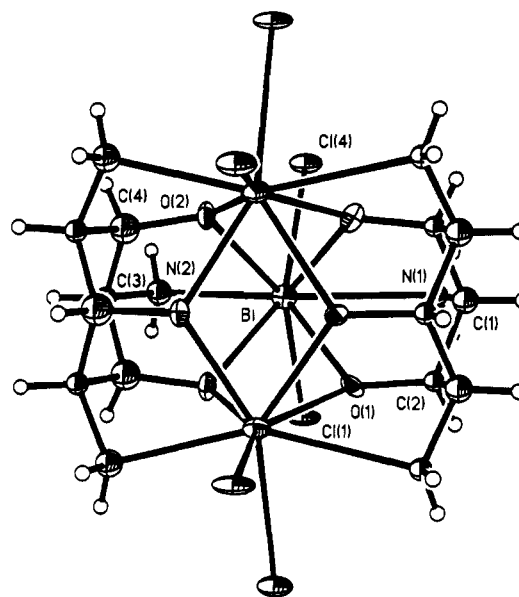
angle	$[\text{Pb}_6(\text{H}_3\text{taci})_2(\text{NO}_3)]^{5+}$		$[\text{Bi}_3(\text{H}_3\text{taci})_2]\text{Cl}_3$	
	av	range	av	range
O–M–O	80.2	78.8(4)–82.5(4)	75.9	73.2(6)–78.6(5)
O–M–O' <sub>cis</sub>			64.3	63.7(4)–64.8(4)
O–M–O' <sub>trans</sub>			108.7	108.6(4)–108.8(5)
O–M–N	70.6	68.3(4)–71.8(5)	68.2	65.9(4)–70.3(5)
O–M–N'			131.3	128.7(6)–134.1(4)
N–M–N'			151.3(7)	
M–O–M	114.5	112.3(5)–117.2(5)	108.5	105.6(4)–111.3(4)
M–O–C	115.1	112.9(10)–116.9(9)	119.7	115.9(15)–123.4(7)
M–N–C	99.9	97.0(11)–101.3(10)	100.5	98.9(11)–102.1(12)
Cl–M–Cl			102.6(1)	
Cl–M–O <sub>cis</sub>			83.2	82.5(2)–84.2(3)
Cl–M–O <sub>trans</sub>			147.5	142.5(3)–152.1(4)
Cl–M–N			81.1	79.6(6)–83.3(4)
O–M–ONO <sub>3</sub> ,bridg	75.5	71.3(4)–79.6(4)		
N–M–ONO <sub>3</sub> ,bridg	135.1	132.9(4)–138.4(4)		

<sup>a</sup> Intraligand angles are indicated as X–M–Y and interligand angles as X–M–Y' (M = Pb, Bi; X, Y = N, O).

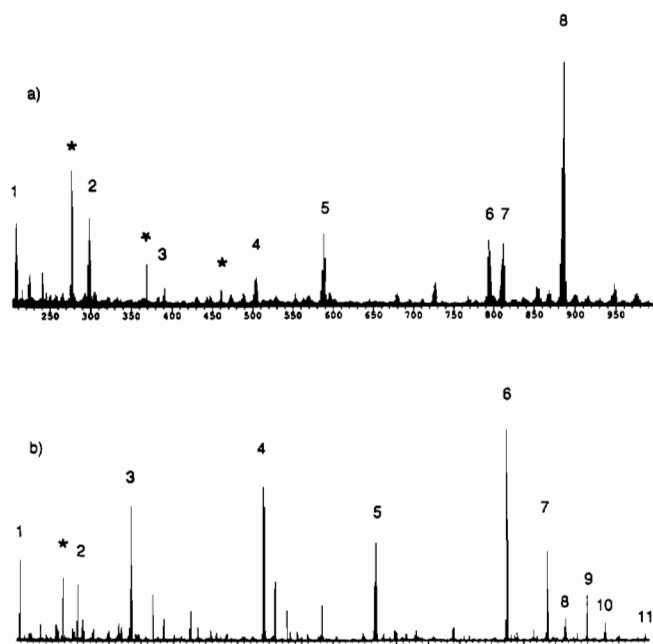
**Figure 1.** Structure of  $[\text{Pb}_6(\text{H}_3\text{taci})_2(\text{NO}_3)]^{5+}$  with numbering scheme and vibrational ellipsoids at the 50% probability level.

of taci were already deprotonated in the compound studied, additional protons must obviously have been abstracted from the  $\text{NH}_2$  groups. It is interesting to note that the two cores  $[\text{Pb}_3(\text{taci}) - x\text{H}]$  and  $[\text{Bi}_3(\text{taci})_2 - y\text{H}]$  remained intact under FAB conditions:  $[\text{Pb}_3(\text{taci})(\text{glycerol}) - 5\text{H}]^+$  and  $[\text{Bi}_3(\text{taci})_2 - 8\text{H}]^+$  were the most intense peaks in the two spectra, whereas the peripheral ligands were easily eliminated or replaced by ligands from the matrix. It is particularly interesting to note that complexes of the dimeric  $[\text{Pb}_3(\text{taci}) - x\text{H}] - \text{O} - \text{NO} - \text{O} - [\text{Pb}_3(\text{taci}) - x\text{H}]$  entity were not observed at all. Thus the mass spectra strongly suggest the presence of stable cores built up from three metal ions and one (Pb) or two (Bi) taci molecules, respectively. Furthermore, the two cores are obviously only weakly bound to additional ligands.

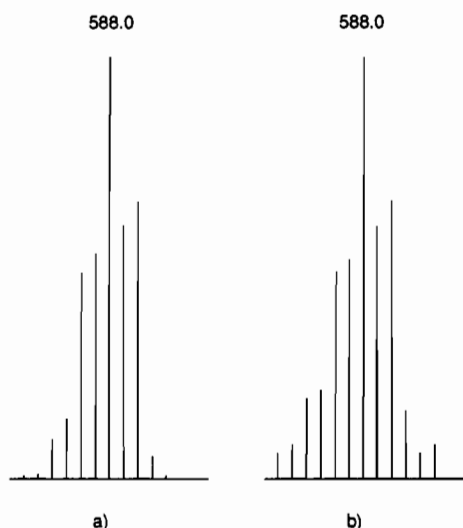
It is well established that the glycerol matrix acts as a strong reducing agent under FAB conditions.<sup>4,6</sup>  $\text{Pb}^+$  is the only reduced species, detected in the spectrum of the Pb compound (Figure

**Figure 2.** Structure of  $[\text{Bi}_3(\text{H}_3\text{taci})_2]\text{Cl}_3$  with numbering scheme and vibrational ellipsoids at the 50% probability level.

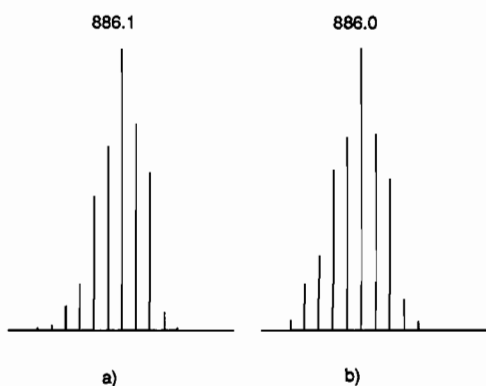
3a). However, in the spectrum of the Bi compound a variety of reduced species such as  $\text{Bi}^+$ ,  $[\text{Bi}(\text{glycerol})]^+$ , and  $[\text{Bi}_2(\text{taci}) - 3\text{H}]^+$  could be assigned. The different reducibility of the Bi and Pb compound under FAB conditions is in agreement with a more pronounced tendency of Bi to form low-valent species.<sup>20</sup> In addition, a careful analysis of the isotope pattern of the molecular ion  $\text{M}^+ = [\text{Bi}_3(\text{taci})_2 - 8\text{H}]^+$  (Figure 6) exhibited intensities for  $[\text{M}^+ + 1]^+$  and  $[\text{M}^+ + 2]^+$  which are significantly higher than expected according to the contribution of <sup>13</sup>C and <sup>15</sup>N of  $\text{M}^+$ . Therefore, these signals must be assigned to additional species  $[\text{Bi}_3(\text{taci})_2 - 7\text{H}]^+$  and  $[\text{Bi}_3(\text{taci})_2 - 6\text{H}]^+$ , i.e., complexes



**Figure 3.** FAB<sup>+</sup> mass spectra of (a)  $[\text{Pb}_6(\text{H}_3\text{taci})_2(\text{NO}_3)](\text{NO}_3)_4(\text{OH})\cdot 2\text{H}_2\text{O}$  and (b)  $[\text{Bi}_3(\text{H}_3\text{taci})_2](\text{NO}_3)_3\cdot 0.5\text{CH}_3\text{OH}$ . The matrix peaks  $[\text{H}(\text{glycerol})_n]^+$  ( $3 \leq n < 5$ ) are indicated with an asterisk. For peak assignments, see Table V.

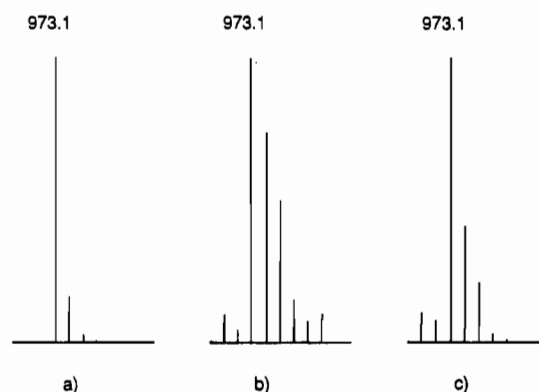


**Figure 4.** (a) Calculated isotope pattern of a 1:2 mixture of  $[\text{Pb}_2(\text{taci}) - 5\text{H}]^+$  and  $[\text{Pb}_2(\text{taci}) - 3\text{H}]^+$ . (b) Measured isotope pattern of peak 5 in Figure 3a.



**Figure 5.** (a) Calculated isotope distribution for  $[\text{Pb}_3(\text{taci})(\text{glycerol}) - 5\text{H}]^+$  and (b) measured isotope pattern of peak 8 in Figure 3a.

containing reduced Bi(II) or Bi(I). Furthermore, a comparison of the spectrum of  $\text{Bi}_3\text{H}_3(\text{taci})_2\text{Cl}_3\cdot 4\text{H}_2\text{O}$  and  $\text{Bi}_3(\text{H}_3\text{taci})_2(\text{NO}_3)_3\cdot 0.5\text{CH}_3\text{OH}$  demonstrates that the amount of reduction



**Figure 6.** (a) Calculated isotope distribution for  $[\text{Bi}_3(\text{taci})_2 - 8\text{H}]^+$ , (b) measured isotope pattern in the FAB<sup>+</sup> mass spectrum of  $[\text{Bi}_3(\text{H}_3\text{taci})_2]\text{Cl}_3\cdot 4\text{H}_2\text{O}$ , and (c)  $[\text{Bi}_3(\text{H}_3\text{taci})_2](\text{NO}_3)_3\cdot 0.5\text{CH}_3\text{OH}$  (peak 6 in Figure 3b).

**Table V.** FAB<sup>+</sup>-MS Data for  $[\text{Pb}_6(\text{H}_3\text{taci})_2(\text{NO}_3)](\text{NO}_3)_4(\text{OH})\cdot 2\text{H}_2\text{O}$  and  $[\text{Bi}_3(\text{H}_3\text{taci})_2](\text{NO}_3)_3\cdot 0.5\text{CH}_3\text{OH}$ , Glycerol (=glyc) Matrix

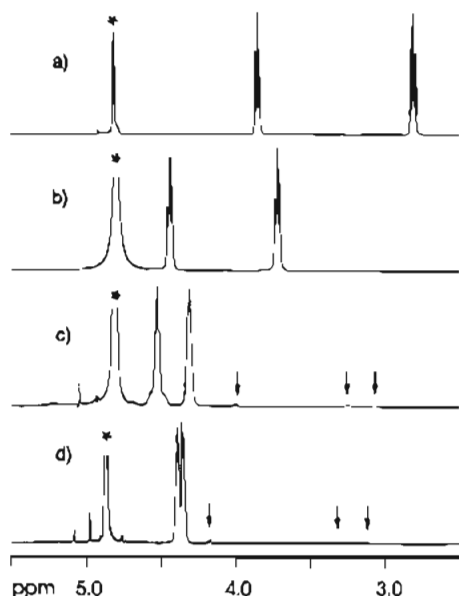
peak no. <sup>a</sup>	assignments	
	Pb complex	Bi complex
1	$[\text{Pb}]^+$	$[\text{Bi}]^+$
2	$[\text{Pb}(\text{glyc}) - \text{H}]^+$	$[\text{Bi}(\text{glyc})]^+$
3	$[\text{Pb}(\text{glyc})_2 - \text{H}]^+$	$[\text{Bi}(\text{taci}) - 2\text{H}]^+$
4	$[\text{Pb}_2(\text{glyc}) - 3\text{H}]^+$	$[\text{Bi}_2(\text{taci}) - 5\text{H}]^+$ $[\text{Bi}_2(\text{taci}) - 3\text{H}]^+$
5 <sup>b</sup>	$[\text{Pb}_2(\text{taci}) - 5\text{H}]^+$ $[\text{Pb}_2(\text{taci}) - 3\text{H}]^+$	$[\text{Bi}_2(\text{taci})_2 - 7\text{H}]^+$ $[\text{Bi}_2(\text{taci})_2 - 5\text{H}]^+$
6 <sup>c</sup>	$[\text{Pb}_3(\text{taci}) - 5\text{H}]^+$	$[\text{Bi}_3(\text{taci})_2 - 8\text{H}]^+$
7	$[\text{Pb}_3(\text{taci})\text{O} - 3\text{H}]^+$	$[\text{Bi}_3(\text{taci})_2(\text{NO}_3) - 7\text{H}]^+$
8 <sup>d</sup>	$[\text{Pb}_3(\text{taci})(\text{glyc}) - 5\text{H}]^+$	$[\text{Bi}_3(\text{taci})_2(\text{glyc}) - 8\text{H}]^+$
9		$[\text{Bi}_3(\text{taci})_2(\text{NO}_3)_2 - 6\text{H}]^+$
10		$[\text{Bi}_3(\text{taci})_2(\text{NO}_3)(\text{glyc}) - 7\text{H}]^+$
11		$[\text{Bi}_3(\text{taci})_2(\text{NO}_3)_2(\text{glyc}) - 6\text{H}]^+$

<sup>a</sup> Referring to Figure 3. <sup>b</sup> See also Figure 4. <sup>c</sup> See also Figure 6. <sup>d</sup> See also Figure 5.

of  $\text{M}^+$  strongly depends on experimental conditions. An analogous reduction of the trinuclear Pb(II) entity has not been observed (Figure 5).

In contrast to the appearance of reduced species in the FAB spectra, the observation of oxidized species by using a glycerol matrix is rather unexpected. However, the detection of  $[\text{Pb}_2(\text{taci}) - 5\text{H}]^+$  (Figure 4) and  $[\text{Bi}_2(\text{taci})_2 - 7\text{H}]^+$  (Figure 3b, peak 5) indicates the formation of a Pb(III) and Bi(IV) complex or (chemically more sensible) the formation of mixed-valence species  $[\text{Pb}^{\text{II}}\text{Pb}^{\text{IV}}(\text{taci}) - 5\text{H}]^+$  and  $[\text{Bi}^{\text{III}}\text{Bi}^{\text{IV}}(\text{taci})_2 - 7\text{H}]^+$ .

<sup>1</sup>H NMR spectra and <sup>13</sup>C NMR spectra of  $[\text{Bi}_3(\text{H}_3\text{taci})_2]\text{Cl}_3\cdot 4\text{H}_2\text{O}$  and  $[\text{Pb}_6(\text{H}_3\text{taci})_2(\text{NO}_3)](\text{NO}_3)_4(\text{OH})\cdot 2\text{H}_2\text{O}$  were measured in neutral D<sub>2</sub>O. The most important result is the observation of only one dominant species in solution. Signals of minor species appeared with less than 5% abundance (Figure 7). The presence of free ligand has not been observed in the complex solutions. Thus, a partial dissociation of the complexes did not occur. The existence of a rapid equilibrium (averaged signals) can be ruled out since the addition of free ligand to solutions of the complex showed the expected signals of uncoordinated taci. The dominant species of the two compounds showed two signals in the <sup>1</sup>H NMR as well as in the <sup>13</sup>C NMR spectra, indicating two sets of equivalent C atoms C(-O) and C(-N), and two sets of equivalent H atoms, H(-CN) and H(-CO). The significant downfield shift for both signals of the <sup>1</sup>H NMR spectrum, compared with the free ligand itself (Figure 7a), is in agreement with the simultaneous binding of the metal to the alkoxo groups and amino groups of taci. The presence of only two signals for each complex does not necessarily imply a high molecular symmetry. It could also be a consequence of fast intramolecular motions. For instance, both a monomeric  $[\text{Pb}_3(\text{H}_3\text{taci})]^{3+}$  ( $\text{C}_{3v}$ ) or a dimeric  $[\text{Pb}_2(\text{H}_3\text{taci})] - \text{O} - \text{NO} - \text{O} - [\text{Pb}_3(\text{H}_3\text{taci})]^{5+}$  ( $\text{C}_{2h}$ )



**Figure 7.**  $^1\text{H}$  NMR spectra ( $\text{D}_2\text{O}$ ) of (a) taci, (b)  $\text{H}_3(\text{taci})(\text{NO}_3)_3$ , (c)  $[\text{Pb}_6(\text{H}_{-3}\text{taci})_2(\text{NO}_3)](\text{NO}_3)_4(\text{OH})\cdot 2\text{H}_2\text{O}$ , and (d)  $[\text{Bi}_3(\text{H}_{-3}\text{taci})_2]\text{Cl}_3\cdot 4\text{H}_2\text{O}$ . The HDO peak is indicated with an asterisk. Minor species are indicated by arrows.

complex with fast rotation around the O–NO bonds are in agreement with the observed spectrum. However, the rather weak binding of  $\text{NO}_3^-$  and  $\text{Cl}^-$  to the complexes, as indicated by the FAB-MS and the IR spectra, and the observation that  $[\text{Bi}_3(\text{H}_{-3}\text{taci})_2]\text{Cl}_3\cdot 4\text{H}_2\text{O}$  and  $[\text{Bi}_3(\text{H}_{-3}\text{taci})_2](\text{NO}_3)_3\cdot 0.5\text{CH}_3\text{OH}$  gave identical NMR spectra are in accordance with the formation of  $[\text{Pb}_3(\text{H}_{-3}\text{taci})]^{3+}_{\text{aq}}(\text{D}_{3h})$  and  $[\text{Bi}(\text{H}_{-3}\text{taci})_2]^{3+}_{\text{aq}}(\text{D}_{3h})$  in aqueous solution. The presence of labile peripheral ligands is also indicated by the facile conversion of  $[\text{Bi}_3(\text{H}_{-3}\text{taci})_2](\text{NO}_3)_3$  to  $[\text{Bi}_3(\text{H}_{-3}\text{taci})_2]\text{Cl}_3$  on the ion-exchange resin.

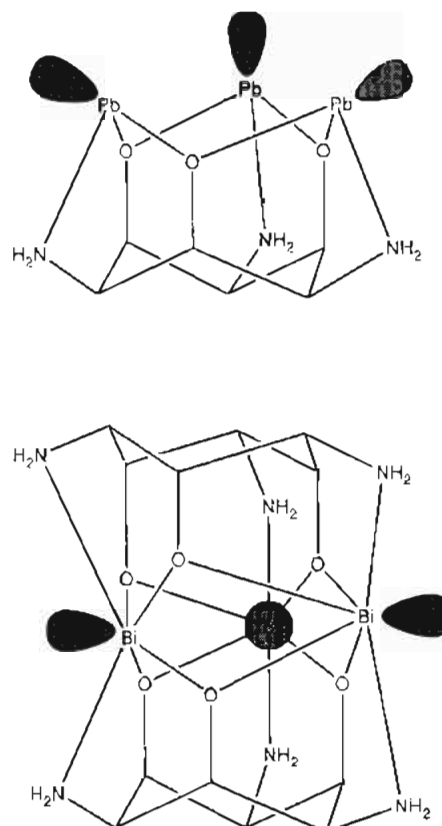
### Conclusions

Taci is obviously a powerful ligand for Pb(II) and Bi(III). The complexes presented in this paper were readily formed and stable in aqueous solutions. No indication of hydrolysis has been observed. However, it is remarkable that solutions containing a molar ratio taci:metal of 2 yield complexes with such a low value as 0.667 (Bi) or 0.333 (Pb). Several aspects must be considered to understand this result.

(a) On the basis of the different steric requirements of five-membered and six-membered chelate rings, a preference of sites ii and iii for large cations ( $d < 1.6 \text{ \AA}$ ) and of sites i and iv for small cations has been postulated.<sup>5,21</sup> However, this cannot be the only reason for the binding of Bi(III) and Pb(II) to site iii, since the large Tl(III)<sup>6</sup> and Ba(II)<sup>22</sup> coordinate to sites i and iv of taci.

(b) The high affinity of Pb(II)<sup>7,23–25</sup> and Bi(III)<sup>8,25,26</sup> for alkoxo groups is well established. Moreover, Pb(II)<sup>7,12,24,27</sup> and Bi(III)<sup>8,28,29</sup> complexes have a pronounced tendency to form polynuclear oxo-, alkoxo-, or hydroxo-bridged species. The

**Chart II**



deprotonated hydroxyl group of taci, bound to one Bi(III) or Pb(II) ion, is obviously more nucleophilic than the hydroxyl group of an additional ligand. Thus, the coordination of additional metal ions to  $\text{M}(\text{H}_1\text{taci})$  and  $\text{M}_2(\text{H}_2\text{taci})$  is a highly favored process.

(c) The “asymmetric” sites ii and iii of taci are particularly suitable to bind metal ions with a stereochemically active lone pair. The short bond distances of Pb(II) and Bi(III) to the donor groups of taci and the long distances to the peripheral ligands,<sup>30</sup> together with the ease to eliminate or substitute the peripheral ligands, clearly indicate the presence of a stereochemically active lone pair in the present complexes (Chart II). Hancock et al. postulated that a change from an inactive to an active lone pair is generally accompanied by a shortening of the Pb–N bond lengths.<sup>31</sup> A comparison of several complexes demonstrated that where the lone pair is active, the Pb–N bond lengths fall in the range of 2.37–2.56  $\text{\AA}$ . On the other hand, in complexes with an inactive lone pair, Pb–N distances of 2.62–2.88 have been reported. The average Pb–N distance of 2.46  $\text{\AA}$  as observed in the present Pb(II) complex clearly falls in the first category.

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**Supplementary Material Available:** Tables SI–SV, listing crystallographic data, anisotropic displacement parameters, positional parameters of hydrogen atoms, bond distances, and bond angles (13 pages). Ordering information is given on any current masthead page. A table of calculated and observed structure factors is available from the authors upon request.

- (21) Angyal, S. J. *Tetrahedron* 1974, 30, 1695.  
 (22) Hegetschweiler, K.; Hancock, R. D.; Ghisletta, M.; Gramlich, V.; Schmalte, H. W. *Inorg. Chem.*, submitted for publication.  
 (23) Keller, H.-L.; Riebe, H.-J. *Z. Anorg. Allg. Chem.* 1987, 550, 102.  
 (24) (a) Goel, S. C.; Chiang, M. Y.; Buhro, W. E. *Inorg. Chem.* 1990, 29, 4640. (b) Gaffney, C.; Harrison, P. G.; King, T. J. *J. Chem. Soc., Chem. Commun.* 1980, 1251.  
 (25) Sawyer, D. T.; Brannan, J. R. *Inorg. Chem.* 1966, 5, 65.  
 (26) Matchett, M. A.; Chiang, M. Y.; Buhro, W. E. *Inorg. Chem.* 1990, 29, 358.  
 (27) Sylva, R. N.; Brown, P. L. *J. Chem. Soc., Dalton Trans.* 1980, 1577.  
 (28) (a) Sundvall, B. *Inorg. Chem.* 1983, 22, 1906. (b) Lazarini, F. *Acta Crystallogr.* 1979, B35, 448. (c) Graunar, M.; Lazarini, F. *Acta Crystallogr.* 1982, B38, 2879. (d) Golic, L.; Graunar, M.; Lazarini, F. *Acta Crystallogr.* 1982, B38, 2881.  
 (29) Sundvall, B. *Acta Chem. Scand.* 1980, A34, 93.

- (30) Drew, M. G. B.; Nicholson, D. G.; Sylte, I.; Vasudevan, A. *Inorg. Chim. Acta* 1990, 171, 11.  
 (31) Hancock, R. D.; Shaikjee, M. S.; Dobson, S. M.; Boeyens, J. C. A. *Inorg. Chim. Acta* 1988, 154, 229.