Inorg. Chem. **2007**, *46*, 4402–4410

Inorganic Chemistry

Article

Influence of pH and Counteranion on the Structure of Tropolonato–Lead(II) Complexes: Structural and Infrared Characterization of Formed Lead Compounds

Krzysztof Lyczko,*,† Wojciech Starosta,† and Ingmar Persson‡

Institute of Nuclear Chemistry and Technology, Dorodna 16, PL-03-195 Warsaw, Poland, and
Department of Chemistry; Swedish University of Agricultural Sciences, P.O. Box 7015,
SE-750 07 Uppsala, Sweden

Received August 17, 2006

Reactions of tropolone with lead(II) trifluoromethanesulfonate, perchlorate, and nitrate in water/methanol mixtures at pH below 1.0 lead to the formation of three different polymeric lead(II) complexes, $[Pb(trop)(CF_3SO_3)(H_2O)]_n$ (**1**), $[Pb_3(trop)_4(ClO_4)_2]_n$ (**2**), and $[Pb_2(trop)_2(NO_3)_2(CH_3OH)]_n$ (**3**), respectively. On the other hand, if the reactions are performed at pH above 2.0, the dimeric compound $[Pb(trop)_2]_2$ (**4**) is obtained independently of the lead(II) salt used, as long as lead(II) does not form any strong complexes with the counterion. The crystal structures of these compounds have been determined by single-crystal X-ray diffraction. The structure of solid tetrakis(tropolonato)-lead(IV), $Pb(trop)_4$ (**5**), has been studied by means of the EXAFS technique because it was not possible to obtain sufficiently large single crystals. In the polymeric structures, the counterions are coordinated to the lead(II) ions and act as bridges. The tropolonato ligand behaves as a chelating agent and a tri- or tetraconnective bridge. The total coordination number of the lead(II) ion is five in compound **4**, seven in **1** and **3**, and eight in **2**, and the lead(IV) ion in **5** is eight-coordinated. The $6s^2$ lone electron pair on the lead(II) ion seems to be stereochemically active in all lead(II) complexes studied. All compounds have been characterized by IR spectroscopy as well.

Introduction

Tropolone (2-hydroxy-2,4,6-cycloheptatriene-1-one), abbreviated as Htrop, is a non-benzenoid aromatic compound in the form of a seven-membered ring. The tropolonato anion is a bidentate ligand, which forms a five-membered chelate ring upon complexation to a metal ion. The functional groups of tropolone (carbonyl and hydroxyl) make it possible to coordinate a number of different metal ions (in oxidation states from +I to +VI). There are many structural data on solids containing only simple tropolonato−metal complexes, e.g., $[Cu(trop)_2]$,[1] $[Sn(trop)_2]$,[2] $[Sc(trop)_3]$,[3] $[In(trop)_3]$,[4] $[Al(trop)_3]$,[5] $[Zr(trop)_4]$,[6] and $[Sn(trop)_4]$.[7] Moreover, some dimeric species, such as $[Ga(trop)(C(SiMe_3)_2)]_2$,[8] $[Al(trop)Et_2]_2$,[9] $[Tl^{III}(trop)Ph_2]_2$,[10] $[Bi^{III}(trop)_2(NO_3)]_2$,[11] and $[Ni(trop)_2H_2O]_2$,[12] and polymeric structures such as $[Zn(trop)_2]_n$[2] and $[Hg(trop)_2]_n$[13] with tropolone have been reported. A large number of other tropolonato−metal and −nonmetal compounds with mixed ligands have been structurally character-

---

* To whom correspondence should be addressed. E-mail: kml@ichtj.waw.pl. Phone: +48 22 5041355. Fax: +48 22 8111532.

† Institute of Nuclear Chemistry and Technology.

‡ Swedish University of Agricultural Sciences.

(1) Hasegawa, M.; Inomaki, Y.; Hoshi, T.; Kobayashi, M. *Inorg. Chim. Acta* **1997**, *257*, 259−264.

(2) Barret, M. C.; Mahon, M. F.; Molloy, K. C.; Steed, J. W.; Wright, P. *Inorg. Chem.* **2001**, *40*, 4384−4388.

(3) Anderson, T. J.; Neuman, M. A.; Melson, G. A. *Inorg. Chem.* **1973**, *12*, 927−930.

(4) Nepveu, F.; Jasanada, F.; Walz, L. *Inorg. Chim. Acta* **1993**, *211*, 141−147.

(5) Muetterties, E. L.; Guggenberger, L. J. *J. Am. Chem. Soc.* **1972**, *94*, 8046−8055.

(6) Davis, A. R.; Einstein, F. W. B. *Acta Crystallogr., Sect. B* **1978**, *34*, 2110−2115.

(7) Kira, M.; Zhang, L. C.; Kabuto, C.; Sakurai, H. *Organometallics* **1998**, *17*, 887−892.

(8) Uhl, W.; Prott, M.; Geiseler, G.; Harms, K. *Z. Naturforsch., B: Chem. Sci.* **2002**, *57*, 141−144.

(9) Lewinski, J.; Zachara, J.; Justyniak, I. *Organometallics* **1997**, *16*, 4597−4605.

(10) Griffin, R. T.; Henrick, K.; Matthews, R. W.; McPartlin, M. *J. Chem. Soc., Dalton Trans.* **1980**, 1550−1555.

(11) Diemer, R.; Keppler, B. K.; Dittes, U.; Nuber, B.; Seifried, V.; Opferkuch, W. *Chem. Ber.* **1995**, *128*, 335−342.

(12) Irving, R. J.; Post, M. L.; Povey, D. C. *J. Chem. Soc., Dalton Trans.* **1973**, 697−701.

(13) Allmann, R.; Dietrich, K.; Musso, H. *Liebigs Ann. Chem.* **1976**, 1185−1198.

10.1021/ic061561f CCC: $37.00

ized, e.g., [Rh^I(CO)(trop)PPh_3],[14] [B(trop)($C_6H_4O_2$)],[15] [Tl^{III}(trop)(CH_3)$_2$],[16] [Sn^{IV}(trop)$_2$$Cl_2$],[17] [$Si^{IV}$(trop)$_2$$Ph_2$],[18] [$Bi^V$(trop)$_2$($C_6H_5CH_3$)$_2$],[19] and [($U^{VI}O_2$)(trop)$_2$py].[20]

Tropolone chelates metal cations usually in an anisobidentate manner, with one shorter and one longer bond to the metal ion. However, equal distances can be found in the case of copper(II),[1] scandium(III),[3] aluminum(III),[5] gallium(III),[8] and thallium(III) tropolonates.[16] Tropolone can also act as a bridging ligand forming triconnective bonding.[2,9−13,21,22]

Recently, tropolone has been extensively studied in respect of its physicochemical properties[23] and biological activity.[24] Tropolone, its derivatives, and their metal chelate compounds have been the subject of numerous investigations. A large number of papers have reported a variety of biological effects, including insecticidal, antifungical, and antimicrobial activity.[11,25]

A vast number of crystallographic studies on compounds between tropolone and p-block elements have been presented.[2,4,5,7−11,15−19,22,26] The methods of synthesis of bis(tropolonato)lead(II), tetrakis(tropolonato)lead(IV), and complexes of other metal cations with tropolone have been reported previously.[27] However, no structural data on any tropolonato−lead compound have been presented until now. The aim of this work was to characterize the structures of some lead(II) and lead(IV) tropolonato complexes prepared from a few starting materials under somewhat different conditions. It was supposed that the composition and the structure of lead(II) complexes may depend on the anion. Since the lead(II) salts are generally weakly soluble or insoluble, a limited number of lead salts could be applied. In this study, the triflate, perchlorate, nitrate, and acetate salts were chosen because of sufficient solubility in the water/methanol mixture used. The acids derived from these anions feature a different acidic strength, with acetic acid being weak, perchloric and nitric acids strong, and triflic acid very strong. In the case of lead(IV), only the acetate was used, as it is the only common and stable source of this oxidation state available.

Experimental Section

Chemicals. In all preparations, tropolone $C_7H_6O_2$ (Aldrich), lead(II) oxide PbO (Fluka), lead(II) perchlorate trihydrate $Pb(ClO_4)_2 \cdot 3H_2O$ (Aldrich), lead(II) nitrate $Pb(NO_3)_2$ (Aldrich), lead(II) acetate trihydrate $Pb(CH_3COO)_2 \cdot 3H_2O$ (Fluka), lead(IV) acetate $Pb(CH_3COO)_4$ (Aldrich), trifluoromethanesulfonic acid CF_3SO_3H (Fluka), perchloric acid $HClO_4$ (aq 70%) (Fluka), methanol CH_3OH (Fluka), ethanol C_2H_5OH (Poch Gliwice), dichloromethane CH_2Cl_2 (Poch Gliwice), and *n*-hexane *n*-C_6H_{14} (Poch Gliwice) were used as purchased.

X-ray Crystallography. X-ray diffraction data reflections were measured at room temperature using a KUMA KM4 four circle diffractometer operating in the $\omega - 2\theta$ mode on carefully selected single crystals not showing peak broadening and peak splitting. There were 3 standard reflections monitored every 200 reflections. Unit cell dimensions and standard deviations were obtained by least-squares fits to 25 reflections in the 2θ range 15−30°. Reflections were processed using profile analysis and corrected for Lorentz factor and polarization effects. An analytical absorption correction was applied. The lead(II) ions were located by Patterson's method using the SHELXLS program.[28] Positional parameters of other non-hydrogen atoms were found in the course of successive refinement using the SHELXL97 program.[29] Positions of hydrogen atoms were calculated using SHELXL97 software and allowed to change according to the riding model.[29] The final refinements on F^2 by the full-matrix least-squares method were performed on positional parameters of all atoms and anisotropic temperature factors of all non-hydrogen atoms and isotropic ones of the hydrogen atoms. Details about the data collections and refinements are given in Table 1.

EXAFS. Lead L_{III}-edge X-ray absorption spectra on **5** were recorded at the wiggler beam line 2-3 at the Stanford Synchrotron Radiation Laboratory (SSRL). The EXAFS station was equipped with a Si [220] double crystal monochromator. SSRL operated at 3.0 GeV and a maximum current of 100 mA. The data collection was performed in transmission mode and at ambient temperature. Higher order harmonics were reduced by detuning the second monochromator to 50% of maximum intensity at the end of the scans. The sample was diluted in boron nitride to give an edge step of about 1 unit in the logarithmic intensity ratio and kept in a 1.5 mm silver frame with Mylar tape windows. The energy scale of the X-ray absorption spectra was calibrated by assigning the first inflection point of the L_{III} edge of a lead foil to 13038.0 eV.[30] Four scans were averaged, giving satisfactory data (k^3-weighted) in the *k* range 2−14 $Å^{-1}$. The EXAFSPAK program package was used for the data treatment.[31]

---

(14) Leipoldt, J. G.; Bok, L. D. C.; Basson, S. S.; Meyer, H. *Inorg. Chim. Acta* **1980**, *42*, 105−108.

(15) Balaban, A. T.; Haiduc, I.; Hopfl, H.; Farfan, N.; Santillan, R. *Main Group Met. Chem.* **1996**, *19*, 385−395.

(16) Chow, Y. M.; Britton, D. *Acta Crystallogr., Sect. B* **1975**, *31*, 1929−1924.

(17) Denekamp, C. I. F.; Evans, D. F.; Slawin, A. M. Z.; Williams, D. J.; Wong, Ch. Y.; Woollins J. D. *J. Chem. Soc., Dalton Trans.* **1992**, 2375−2382.

(18) Kira, M.; Zhang, L. C.; Kabuto, C.; Sakurai, H. *Chem. Lett.* **1995**, 659−661.

(19) Dittes, U.; Keppler, B. K.; Nuber, B. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 67−68.

(20) Degetto, S.; Marangoni, G.; Bombieri, G.; Forsellini, E.; Baracco, L.; Graziani, R. *J. Chem. Soc., Dalton Trans.* **1974**, 1933−1939.

(21) Irving, R. J.; Post, M. L.; Baker, R. W. *J. Chem. Soc., Dalton Trans.* **1975**, 1898−1902.

(22) Rettig, S. J.; Storr, A.; Trotter, J. *Can. J. Chem.* **1984**, *62*, 1705−1708.

(23) (a) Mó, O.; Yáñez, M.; Esseffar, M.; Herreros, M.; Notario, R.; Abboud, J. L. -M. *J. Org. Chem.* **1997**, *62*, 3200−3207. (b) MacKenzie, V. J.; Sinha, H. K.; Wallace, S. C.; Steer, R. P. *Chem. Phys. Lett.* **1999**, *305*, 1−7. (c) Shoute, L. C. T.; MacKenzie, V. J.; Falk, K. J.; Sinha, H. K.; Warsylewicz, A; Steer, R. P. *Phys. Chem. Chem. Phys.* **2000**, *2*, 1−9. (d) Casadesús, R.; Vendrell, O.; Moreno, M.; Lluch, J. M. *Chem. Phys. Lett.* **2005**, *405*, 187−192.

(24) (a) Morita, Y.; Matsumura, E.; Okabe, T.; Shibata, M.; Sugiura, M.; Ohe, T.; Tsujibo, H.; Ishida, N.; Inamori, Y. *Biol. Pharm. Bull.* **2003**, *26*, 1487−1490. (b) Doulias, P.-T.; Nousis, L.; Zhu, B.-Z.; Frei, B.; Galaris, D. *Free Radical Res.* **2005**, *39*, 125−135.

(25) (a) Miyamoto, D.; Kusagaya, Y.; Endo, N.; Sometani, A.; Takeo, S.; Suzuki, T.; Arima, Y.; Nakajima, K.; Suzuki, Y. *Antiviral Res.* **1998**, *39*, 89−100. (b) Morita, Y.; Matsumura, E.; Tsujibo, H.; Yasuda, M.; Okabe, T.; Sakagami, Y.; Kumeda, Y.; Ishida, N.; Inamori, Y. *Biol. Pharm. Bull.* **2002**, *25*, 981−985. (c) Nomiya, K.; Yoshizawa, A.; Kasuga, N. C.; Yokoyama, H.; Hirakawa, S. *Inorg. Chim. Acta* **2004**, *357*, 1167−1176.

(26) Park, J. J; Collins, D. M.; Hoard, J. L. *J. Am. Chem. Soc.* **1970**, *92*, 3636−3644.

(27) (a) Muetterties, E. L.; Wright, C. M. *J. Am. Chem. Soc.* **1964**, *86*, 5132−5137. (b) Muetterties, E. L.; Roesky, H.; Wright, C. M. *J. Am. Chem. Soc.* **1966**, *88*, 4856−4861.

(28) Sheldrick, G. M. *Acta Crystallogr., Sect. A* **1990**, *46*, 467−473.

(29) Sheldrick, G. M. *SHELXL97: Program for Crystal Structure Refinement*; University of Göttingen: Göttingen, Germany, 1997.

Table 1. Crystal Data and Structure Refinement Details for Compounds **1**, **2**, **3**, and **4**

	1	**2**	**3**	**4**
chemical formula	$C_8H_7F_3O_6SPb$	$C_{14}H_{10}ClO_8Pb_{1.5}$	$C_{15}H_{14}N_2O_{11}Pb_2$	$C_{14}H_{10}O_4Pb$
fw	495.39	652.46	812.66	449.41
T (K)	293(2)	293(2)	293(2)	293(2)
λ (Mo Kα) (Å)	0.71073	0.71073	0.71073	0.71073
cryst syst	triclinic	monoclinic	triclinic	monoclinic
space group	$P\bar{1}$	$P2/n$	$P\bar{1}$	$P2_1/n$
a (Å)	7.6850(15)	12.030(2)	7.4220(15)	4.9520(10)
b (Å)	8.2317(16)	9.0607(18)	10.171(2)	10.753(2)
c (Å)	9.959(2)	14.652(3)	12.872(3)	23.947(5)
α (deg)	84.92(3)	90.00	90.30(3)	90.00
β (deg)	77.81(3)	101.72(3)	97.11(3)	95.67(3)
γ (deg)	87.29(3)	90.00	94.97(3)	90.00
V (Å^3)	613.1(2)	1563.7(5)	960.5(3)	1268.9(4)
Z	2	4	2	4
D_{calcd} (g·cm^{-3})	2.683	2.771	2.810	2.353
μ (mm^{-1})	13.987	16.360	17.570	13.302
F(000)	456	1192	740	832
cryst size (mm^3)	0.40 × 0.12 × 0.09	0.60 × 0.31 × 0.22	0.37 × 0.35 × 0.22	0.37 × 0.22 × 0.06
reflns collected	3839	3906	5080	2676
indep reflns	3579 [R(int) = 0.0259]	3731 [R(int) = 0.0913]	4765 [R(int) = 0.0686]	2423 [R(int) = 0.0585]
data/restraints/params	3579/2/179	3731/0/224	4765/1/273	2423/0/173
GOF	1.065	1.009	0.971	1.088
final R indices [$I > 2\sigma$] R1,[a] wR2[b]	0.0403, 0.1046	0.0474, 0.1252	0.0490, 0.1374	0.0661, 0.1893
Largest diff. peak/ hole (e·Å^{-3})	3.89 (0.80 Å from Pb1)/ −3.61 (0.83 Å from Pb1)	3.44 (0.83 Å from Pb2)/ −3.59 (0.91 Å from Pb2)	4.21 (0.78 Å from Pb1)/ −3.06 (0.90 Å from Pb2)	2.61 (1.14 Å from Pb1)/ −2.56 (1.42 Å from Pb1)

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$.

Other Methods. Far- and mid-infrared absorption spectra of the compounds were recorded at room temperature with a Bruker Equinox 55 FT-IR spectrometer. Spectra in the range 400−4000 cm^{-1} at a resolution of 1 cm^{-1} were recorded using KBr pellets, and in the range 200−600 cm^{-1} at the resolution of 4 cm^{-1} using CsI pellets. UV−vis spectra of methanol solutions were recorded with a DU-68 Beckman spectrophotometer. ^{1}H and ^{13}C NMR spectra of saturated solutions were measured on a Bruker DRX 400 MHz or a Varian Unity Plus 500 MHz spectrometer.

Preparations. Lead(II) Trifluoromethanesulfonate (Lead(II) Triflate), $Pb(CF_3SO_3)_2$. Lead(II) oxide was refluxed with an excess of trifuoromethanesulfonic acid until a clear liquid phase was obtained. The excess of water and acid was evaporated off in an oven at 455 K until a white dry powder of anhydrous lead(II) trifluoromethanesulfonate was obtained. Because of its hygroscopic properties, lead(II) triflate should be stored in an oven at 455 K or in an airtight vessel in a desiccator. IR: (KBr pellet, cm^{-1}): 1276sh $\nu_{as}(SO_3)$, 1250vs $\nu_s(CF_3)$, 1172 m $\nu_{as}(CF_3)$, 1049 m $\nu_{as}(SO_3)$, 767vw $\delta_s(CF_3)$, 656 m $\delta_s(SO_3)$, 579vw $\delta_{as}(SO_3)$, 521w $\delta_{as}(CF_3)$; assignments based on ref 57b.

$[Pb(trop)(CF_3SO_3)(H_2O)]_n$ (1). Lead(II) triflate (0.201 g, 0.398 mmol) was dissolved in water (0.5 mL); pH = 2.7. A methanol solution (0.5 mL) of tropolone (0.102 g, 0.835 mmol) was added to the aqueous solution (pH of the mixture decreased below 1), and the reaction mixture was kept in refrigerator. After a few days, brown rodlike crystals (mp 380−383 K) suitable for X-ray crystallography were obtained. Yield: 0.085 g, 43%. Elemental analysis was unsuccessful. UV−vis: λ_{max} (ϵ, dm^3·mol^{-1}·cm^{-1}) = 234 (32900), 324 (13325), 386 (4775) nm. ^{1}H NMR (CD$_3$OD): δ = 7.13 [t, 1H, H$_5$], 7.31 [d, 2H, H$_{3,7}$], 7.60 [t, 2H, H$_{4,6}$] ppm. ^{13}C NMR (CD$_3$OD): δ = 120.6 [CF$_3$], 129.1 [C$_5$], 130.1 [C$_{4,6}$], 139.3 [C$_{3,7}$], 182.2 [br, C$_1$, C$_2$] ppm.

$[Pb_3(trop)_4(ClO_4)_2]_n$ (2). An aqueous solution of lead(II) perchlorate was prepared by the following methods: (a) Lead(II) oxide (0.0776 g, 0.348 mmol) was dissolved in perchloric acid (0.4 mL; ∼ 15%), pH of solution was below 1. A methanol solution (0.4 mL) of tropolone (0.0938 g, 0.768 mmol) was added to the aqueous lead(II) solution, and an orange crystalline product (mp > 533 K) was formed. Yield: 0.069 g, 46%. (b) Lead(II) perchlorate trihydrate (0.386 g, 0.839 mmol) was dissolved in water (0.9 mL); pH = 3.2. At the addition of a methanol solution (0.9 mL) of tropolone (0.210 g, 1.720 mmol), a yellow compound of bis(tropolonato)lead(II) precipitated immediately, and the pH of the reaction mixture decreased below 1. In a few hours, the bis(tropolonato)lead(II) was transformed into orange crystals with the same composition as those in preparation route (a) described above. Yield: 0.300 g, 82%. Anal. Calcd for $C_{14}H_{10}ClO_8Pb_{1.5}$: C, 25.77; H, 1.54. Found: C, 25.89; H, 2.00. UV−vis: λ_{max} (ϵ, dm^3·mol^{-1}·cm^{-1}) = 234 (41975), 324 (17475), 385 (6975) nm. ^{1}H NMR (CD$_3$OD): δ = 7.14 [t, 1H, H$_{5,15}$], 7.30 [d, 2H, H$_{3,7}$ (H$_{13,17}$)], 7.59 [t, 2H, H$_{4,6}$ (H$_{14,16}$)] ppm. ^{13}C NMR (CD$_3$OD): δ = 127.2 [C$_5$ (C$_{15}$)], 129.1 [C$_{4,6}$ (C$_{14,16}$)], 137.4 [C$_{3,7}$ (C$_{13,17}$)] ppm.

Warning: *The compounds of perchlorate salts can be explosive and should be treated with great caution.*

$[Pb_2(trop)_2(NO_3)_2(CH_3OH)]_n$ (3). An aqueous solution (0.25 mL) of lead(II) nitrate (0.126 g, 0.380 mmol), pH = 2.8, and a methanol solution (0.25 mL) of tropolone (0.106 g, 0.868 mmol) were mixed, and the resulting mixture (pH < 1) was kept in a refrigerator. At first, very thin fragile yellow foil-like crystals, which could not be used for X-ray measurements, appeared. A part of this crystalline product was recrystallized from methanol before a few orange crystals (mp 521−525 K) suitable for X-ray measurements were obtained. The other part, stored in methanol, gave an orange solid of **3** with time. Yield: 0.111 g, 72%. Anal. Calcd for $C_{15}H_{14}N_2O_{11}Pb_2$: C, 22.17; H, 1.74; N, 3.45. Found: C, 22.05; H, 2.17; N, 3.54. UV−vis: λ_{max} (ϵ, dm^3·mol^{-1}·cm^{-1}) = 234 (63575), 323 (29375), 386 (10775) nm. ^{1}H NMR (CD$_3$OD): δ = 7.14 [t,

---

(30) Thompson, A.; Attwood, D.; Gullikson, E.; Howells, M.; Kim, K.-J.; Kirz, J.; Kortright, J.; Lindau, I.; Pianatta, P.; Robinson, A.; Scofield, J.; Underwood, J.; Vaughan, D.; Williams, G.; Winick, H. *X-ray Data Booklet*, LBNL/PUB-490 Rev. 2; Lawrence Berkeley National Laboratory: Berkeley, CA, 2001.

(31) George, G. N.; Pickering, I. J. *EXAFSPAK*—A Suite of Computer Programs for Analysis of X-Ray Absorption Spectra; SSRL: Stanford, CA, 1993.

1H, $H_{5,15}$], 7.32 [d, 2H, $H_{3,7}$ ($H_{13,17}$)], 7.65 [t, 2H, $H_{4,6}$ ($H_{14,16}$)] ppm. ^{13}C NMR (CD_3OD): $\delta = 128.6$ [C_5 (C_{15})], 130.4 [$C_{4,6}$ ($C_{14,16}$)], 138.8 [$C_{3,7}$ ($C_{13,17}$)], 183.4 [$C_{1,2}$ ($C_{11,12}$)] ppm.

Bis(tropolonato)lead(II), [Pb(trop)$_2$]$_2$ (4). (a) Lead(II) acetate trihydrate (0.172 g, 0.453 mmol) was dissolved in water (1.0 mL); pH = 5.8. A methanol solution (0.4 mL) of tropolone (0.114 g, 0.934 mmol) was added to the aqueous solution (pH of mixture 3.3), and the precipitation of the yellow title compound immediately took place. The bis(tropolonato)lead(II) compound was filtrated off and washed several times with water and ethanol in order to remove the excess of tropolone. Yield: 0.155 g, 76%. Anal. Calcd for $C_{14}H_{10}O_4Pb$: C, 37.42; H, 2.24. Found: C, 37.56; H, 2.56. UV−vis: λ_{max} (ϵ, $dm^3 \cdot mol^{-1} \cdot cm^{-1}$) = 232 (29075), 330 (12000), 386 (5000) nm. ^{1}H NMR (CD_3OD): $\delta = 7.00$ [t, 1H, $H_{5,15}$], 7.19 [d, 2H, $H_{3,7}$ ($H_{13,17}$)], 7.50 [t, 2H, $H_{4,6}$ ($H_{14,16}$)] ppm. ^{13}C NMR (CD_3OD): $\delta = 127.2$ [C_5 (C_{15})], 129.3 [$C_{4,6}$ ($C_{14,16}$)], 138.4 [$C_{3,7}$ ($C_{13,17}$)], 182.9 [$C_{1,2}$ ($C_{11,12}$)] ppm. Crystals of sufficient quality for X-ray diffraction could be grown by slow diffusion of *n*-hexane into a dichloromethane solution of **4**. Using this method, yellow fragile platelike crystals (mp 487−490 K) were formed. (b) Bis(tropolonato)lead(II) can be also synthesized in the same way as described above for lead(II) trifluoromethanesulfonate, perchlorate, and nitrate as starting materials, if the pH of the reaction mixture is maintained above 2.0; see also preparation of **2**, part (b).

Tetrakis(tropolonato)lead(IV), Pb(trop)$_4$ (5). This compound was obtained by mixing a dichloromethane solution (1.5 mL) of lead(IV) acetate (0.227 g, 0.512 mmol) and a methanol solution (0.5 mL) of tropolone (0.338 g, 2.768 mmol). Product **5** precipitated immediately as a brown-violet solid, which is insoluble in common organic solvents. Yield: 0.219 g, 63%. Anal. Calcd for $C_{28}H_{20}O_8Pb$: C, 48.62; H, 2.92. Found: C, 48.17; H, 3.26. UV−vis: λ_{max} (ϵ, $dm^3 \cdot mol^{-1} \cdot cm^{-1}$) = 233.5 (>65500), 328 (>27700), 369sh (>12700) 386sh (>10250) nm (real ϵ values are higher because not all of the compound dissolved in CH_3OH). ^{1}H NMR (CD_3OD): $\delta = 7.06$ [t, 1H], 7.28 [d, 2H], 7.48 [t, 2H] ppm. ^{13}C NMR (CD_2Cl_2): $\delta = 137.8$ ppm.

Results and Discussion

Crystal Structures. [Pb(trop)(CF_3SO_3)(H_2O)]$_n$ (1). The obtained compound has a "steplike" polymeric structure with a repeated sequence of the [Pb(trop)(CF_3SO_3)(H_2O)] formula unit (Figure 1). The unit cell of **1** contains one [Pb(trop)(CF_3SO_3)(H_2O)]$_2$ dimeric unit. The structure can be described as a connection of these dimeric units into polymeric chains. Each lead(II) ion is surrounded by seven oxygen atoms. Two of them belong to the tropolonato ligand, which forms a five-membered chelate ring. There are also two oxygen atoms from two neighboring tropolonato ligands in the polymeric chain, two from two triflate groups, and one from the water molecule. The Pb−O bond distances are in the range 2.29−2.85 Å. The shortest metal−oxygen bonds, 2.293(5) and 2.338(5) Å, are those within the chelate ring; a slightly longer bond, 2.463(6) Å, is that to water. Considerably longer Pb−O bonds of about 2.78 Å from the CF_3SO_3 groups, and from two neighboring tropolonato ligands, 2.763(4) and 2.853(5) Å, complete the coordination sphere around lead(II). All of these lead−oxygen distances are much shorter than the commonly accepted sum of van der Waals radii of lead(II) and oxygen, 3.44 Å.[32]

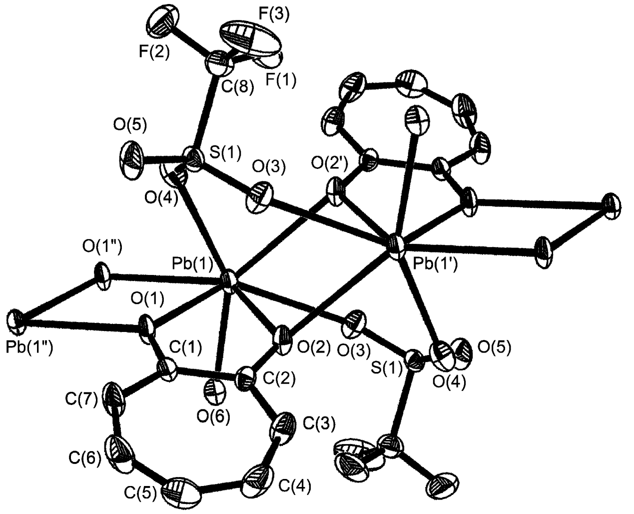

Figure 1. Fragment of the polymeric chain formed by **1**. Selected bond lengths (Å), distances (Å), and angles (deg) are as follows: Pb(1)−O(1) 2.338(5), Pb(1)−O(2) 2.293(5), Pb(1)−O(3) 2.776(5), Pb(1)−O(4) 2.784(6), Pb(1)−O(6) 2.463(6), Pb(1)−O(2′) 2.853(5), Pb(1)−O(1″) 2.763(4), O(1)−C(1) 1.287(7), O(2)−C(2) 1.280(8), Pb(1)···Pb(1′) 4.064(1), Pb(1)···Pb(1″) 4.271(1), O(1)−Pb(1)−O(2) 68.37(16), C(1)−O(1)−Pb(1) 118.31(37), C(2)−O(2)−Pb(1) 119.65(38), O(1)−Pb(1)−O(1″) 66.55(19), O(2)−Pb(1)−O(2′) 76.22(18), O(1)−Pb(1)−O(6) 79.12(19), O(2)−Pb(1)−O(6) 85.11(19), O(4)−Pb(1)−O(6) 148.18(18), O(3)−Pb(1)−O(6) 74.42(18), O(1″)−Pb(1)−O(2′) 139.70(15). The atoms are shown as the 30% probability ellipsoids. Hydrogen atoms are omitted.

Each tropolonato ligand is attached to one lead center with a bite angle of 68.37(16)° and is, in addition, bridging through two of its oxygen atoms to two adjacent lead(II) ions. The tropolonato ligand behaves as a trimetallic tetraconnective bridge in this structure. The bridging Pb−O$_{(trop)}$ bond distances (2.763(4) and 2.853(5) Å) are significantly weaker than the chelating bonds (2.293(5) and 2.338(5) Å). Within each tropolone molecule, approximately equivalent carbon−oxygen bonds of about 1.28 Å are identified. These bond lengths are intermediate between those observed for single C−O (1.33 Å) and double C=O (1.26 Å) bonds in the free tropolone.[33] Moreover, two triflate ions act as bridging groups between two neighboring lead atoms. In one lead(II) complex, where the $CF_3SO_3^-$ ion plays the same role as in **1**, the Pb−O$_{(triflate)}$ bonds are somewhat longer, 2.92 and 2.99 Å.[34a] Only a few examples where triflate groups coordinate lead(II) ions are known.[34] The Pb−O$_{(triflate)}$ bond distances vary in the range 2.48−2.99 Å. In these cases, CF_3SO_3 moieties are connected to lead(II) ions in the monodentate fashion apart from two examples where they bridge in a μ_2 or μ_3 mode.[34]

In the polymeric [Pb(trop)(CF_3SO_3)(H_2O)]$_n$ compound, a nonspherical distribution of ligands around the lead(II) cation

---

(32) Bondi, A. *J. Phys. Chem.* **1964**, *68*, 441−451.

(33) Shimanouchi, H.; Sasada, Y. *Acta Crystallogr., Sect. B* **1973**, *29*, 81−90.

(34) (a) Garcia, A. M.; Romero-Salguero, F. J.; Bassani, D. M.; Lehn, J.-M.; Baum, G.; Fenske, D. *Chem.*−*Eur. J.* **1999**, *5*, 1803−1808. (b) Garcia, A. M.; Bassani, D. M.; Lehn, J. -M.; Baum, G.; Fenske, D. *Chem.*−*Eur. J.* **1999**, *5*, 1234−1238. (c) Nagayama, S.; Kobayashi, S. *J. Am. Chem. Soc.* **2000**, *122*, 11531−11532. (d) De Lima, G. M.; Duncalf, D. J.; Constantine, S. P. *Main Group Met. Chem.* **2000**, *23*, 307−310. (e) Barboiu, M.; Petit, E.; Vaughan, G. *Chem.*−*Eur. J.* **2004**, *10*, 2263−2270. (f) Stadler, A. -M.; Kyritsakas, N.; Lehn, J.-M. *Chem. Commun.* **2004**, 2024−2025.

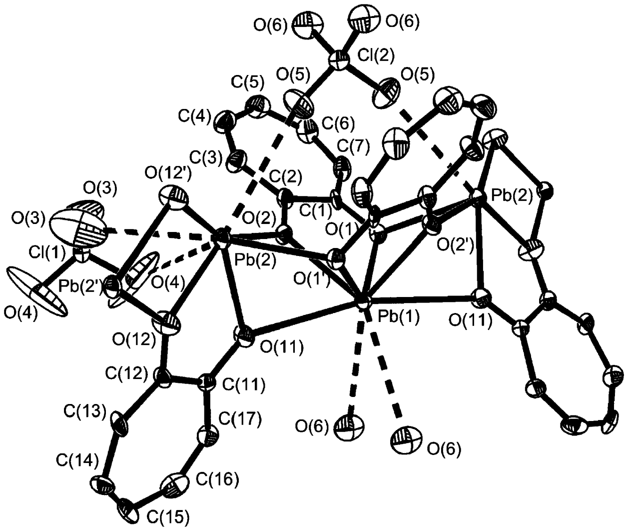

Figure 2. Structure of **2**. Selected bond lengths (Å), distances (Å), and angles (deg) are as follows: Pb(1)−O(1) 2.460(9), Pb(1)−O(2) 2.345(9), Pb(1)−O(11) 2.845(9), Pb(2)−O(11) 2.294(10), Pb(2)−O(12) 2.351(10), Pb(2)−O(1) 2.433(9), Pb(2)−O(2) 2.612(9), Pb(2)−O(12′) 2.725(10), Pb(1)···O(6) 3.170(13), Pb(2)···O(5) 3.372(12), Pb(2)···O(3) 3.111(33), Pb(2)···O(4) 3.026(37), Pb(1)···Pb(2) 3.766(1), Pb(2)···Pb(2′) 4.231(1), O(1)−Pb(1)−O(2) 64.95(29), O(11)−Pb(2)−O(12) 67.27(34), Pb(1)−O(1)−C(1) 118.22(72), Pb(1)−O(2)−C(2) 122.83(78), Pb(2)−O(11)−C(11) 118.19(78), Pb(2)−O(12)−C(12) 117.84(77), Pb(2)−O(12)−Pb(2′) 112.70(40), Pb(1)−O(11)−Pb(2) 93.63(32), Pb(1)−O(1)−Pb(2) 100.64(32), Pb(1)−O(2)−Pb(2) 98.72(32), O(1)−Pb(1)−O(2′) 75.28(32), O(1)−Pb(2)−O(2′) 71.07(29), O(2)−Pb(2)−O(11) 67.47(30), O(1)−Pb(2)−O(11) 73.99(33). The atoms are shown as the 30% probability ellipsoids. Hydrogen atoms are omitted. The distances between lead atoms and oxygens of perchlorate ions are distinguished by means of dotted lines. ADPs parameters for oxygens of Cl(1)O_4^- ion are higher than for Cl(2)O_4^- ion which suggests existing dynamical disorder of first perchlorate group.

is observed (the so-called hemidirected geometry),[35] which results in the presence of a void. This gap in the coordination sphere of lead(II) can be considered as evidence for the presence of a stereochemically active $6s^2$ lone electron pair. The coordination polyhedron around the lead center in the polymeric structure can be regarded as a very distorted square antiprism with one corner occupied by the lone electron pair.

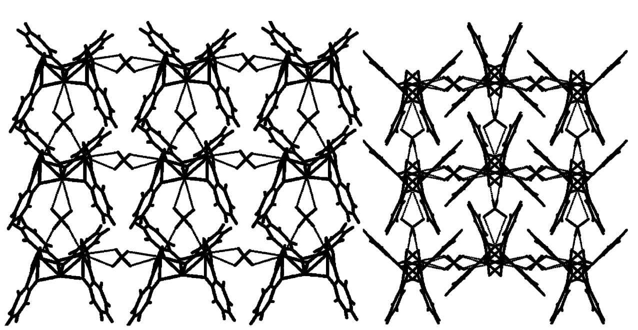

Figure 3. Wireframe view of fragments of structure **2** showing a projection of a three-dimensional net.

[Pb_3(trop)$_4$(ClO_4)$_2$]$_n$ (2). Compound **2** has a polymeric structure which consists of chains formed by repetition of a [Pb_3(trop)$_4$(ClO_4)$_2$] fragment with two types of lead positions, Pb(1) and Pb(2) (Figure 2). The lead(II) ion of the first type, Pb(1), forms two five-membered rings with two tropolonato ligands with bond lengths 2.345(9) and 2.460(9) Å, and two bridging bonds, 2.845(9) Å (Pb(1)−O(11)), with the oxygen atoms from neighboring tropolonato ligands. The lead(II) ion of the second type, Pb(2), forms only one chelate ring with bond lengths 2.294(10) and 2.351(10) Å and three bridges with neighboring tropolonato ligands with distances of 2.433(9) Å (Pb(2)−O(1)), 2.612(9) Å (Pb(2)−O(2)), and 2.725(10) Å (Pb(2)−O(12′)). As in **1,** each tropolonato ligand behaves as a trimetallic tetraconnective bridge. The important components of the structure **2** are the perchlorate anions, which use all their oxygen atoms to connect the individual chains into the large three-dimensional net (Figure 3). Two groups of ClO_4^- ions, with respect to their coordination modes, can be distinguished. The ClO_4^- anion of the first group builds a bridge between three lead(II) ions (two Pb(2) belonging to the same Pb_3(trop)$_4$ unit and one Pb(1) from the neighboring chain lying above) with Pb−O distances of 3.170(13) Å (Pb(1)−O(6)) and 3.372(12) Å (Pb(2)−O(5)). The ClO_4^- ion of the second kind connects, in a bidentate way, two Pb(2) atoms which are situated on two adjacent chains with distances of 3.026(37) Å (Pb(2)−O(4)) and 3.111(33) Å (Pb(2)−O(3)). The Cl(1)O_4^- and Cl(2)O_4^- ions behave in structure **2** as μ_2- and μ_3-*O,O′,O″,O‴*-bridging agents, respectively. In a number of papers, it was found that the perchlorate groups can interact with lead(II) ions as monodentate,[36,37] bidentate chelating,[37,38] *O,O′*-bridging,[37,39] *O,O′,O″*-bridging,[40] *O,O,O′*-bridging,[41] and *O,O,O′,O″*-bridging[37c] ligands. The range of distances between the lead(II) ion and the oxygen atoms from the perchlorate ions is very wide. In some cases, these contacts can be as short as 2.60, 2.69,[38b,42] and 2.70 Å[39] whereas in other cases as long as 3.20,[37c] 3.21,[37a] 3.29,[40] and 3.37 Å.[43]

In comparison with Pb−O$_{(trop)}$ bond lengths in **2** (2.29−2.84 Å), the Pb−O$_{(ClO4)}$ distances are significantly longer (3.03−3.37 Å), and they should be considered as long contacts. However, all these Pb−O distances are shorter than

---

(35) Shimoni-Livny, L.; Glusker, J. P.; Bock, Ch. W. *Inorg. Chem.* **1998**, *37*, 1853−1867.

(36) (a) Küppers, H.-J.; Wieghardt, K.; Nuber, B.; Weiss, J. *Z. Anorg. Allg. Chem.* **1989**, *577*, 155−164. (b) Esteban, D.; Banobre, D.; de Blas, A.; Rodriguez-Blas, T.; Bastida, R.; Macias, A.; Rodriguez, A.; Fenton, D. E.; Adams, H.; Mahia, J. *Eur. J. Inorg. Chem.* **2000**, 1445−1456. (c) Le Derf, F.; Mazari, M.; Mercier, N.; Levillain, E.; Trippe, G.; Riou, A.; Richomme, P.; Becher, J.; Garin, J.; Orduna, J.; Gallego-Planas, N.; Gorgues, A.; Salle, M. *Chem.*−*Eur. J.* **2001**, *7*, 447−455.

(37) (a) Harrowfield, J. M.; Skelton, B. W.; White, A. H. *J. Chem. Soc., Dalton Trans.* **1993**, 2011−2016. (b) Aragoni, M. C.; Arca, M.; Demartin, F.; Devillanova, F. A.; Isaia, F.; Garau, A.; Lippolis, V.; Jalali, F.; Papke, U.; Shamsipur, M.; Tei, L.; Yari, A.; Verani, G. *Inorg. Chem.* **2002**, *41*, 6623−6632. (c) Thompson, L. K.; Zhao, L.; Xu, Zh.; Miller, D. O.; Reiff, W. M. *Inorg. Chem.* **2003**, *42*, 128−139.

(38) (a) Bytheway, I.; Engelhardt, L. M.; Harrowfield, J. M.; Kepert, D. L.; Miyamae, H.; Patrick, J. M.; Skelton, B. W.; Soudi, A. A.; White, A. H. *Aust. J. Chem.* **1996**, *49*, 1099−1110. (b) Beer, P. D.; Drew, M. G. B.; Gale, P. A.; Ogden, M. I.; Powell, H. R. *CrystEngComm* **2000**, *2*, 164−168.

(39) Blake, A. J.; Fenske, D.; Li, W.-Sh.; Lippolis, V.; Schroder, M. *J. Chem. Soc., Dalton Trans.* **1998**, 3961−3968.

(40) Engelhardt, L. M.; Harrowfield, J. M.; Miyamae, H.; Patrick, J. M.; Skelton, B. W.; Soudi, A. A.; White, A. H. *Aust. J. Chem.* **1996**, *49*, 1111−1119.

(41) Tei, L.; Blake, A. J.; Bencini, A.; Valtancoli, B.; Wilson, C.; Schroder, M. *Inorg. Chim. Acta* **2002**, *337*, 59−68.

(42) Adam, K. R.; Baldwin, D. S.; Bashall, A.; Lindoy, L. F.; McPartin, M.; Powell, H. R. *J. Chem. Soc., Dalton Trans.* **1994**, 237−238.

(43) Harrowfield, J. M.; Miyamae, H.; Shand, T. M.; Skelton, B. W.; Soudi, A. A.; White, A. H. *Aust. J. Chem.* **1996**, *49*, 1051−1066.

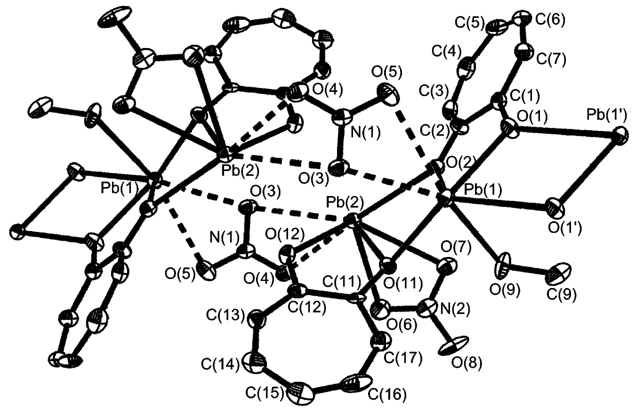

Figure 4. Structure of **3**. Selected bond lengths (Å), distances (Å), and angles (deg) are as follows: Pb(1)−O(1) 2.346(9), Pb(1)−O(2) 2.317(9), Pb(1)−O(3) 2.672(9), Pb(1)−O(5) 2.821(11), Pb(1)−O(9) 2.559(10), Pb(1)−O(11) 2.597(8), Pb(1)−O(1′) 2.769(8), Pb(2)−O(11) 2.361(9), Pb(2)−O(12) 2.350(9), Pb(2)−O(3) 3.010(9), Pb(2)−O(4) 2.868(10), Pb(2)−O(6) 2.569(11), Pb(2)−O(7) 2.805(10), Pb(2)−O(2) 2.758(8), O(1)−C(1) 1.307(14), O(2)−C(2) 1.277(14), O(11)−C(11) 1.280(13), O(12)−C(12) 1.302(14), Pb(1)···Pb(2) 4.076(1), Pb(1)···Pb(1′) 4.317(1), Pb(2)···Pb(2) 4.128(2), O(1)−Pb(1)−O(2) 67.43(28), O(11)−Pb(2)−O(12) 67.29(29), O(2)−Pb(1)−O(11) 69.83(28), O(2)−Pb(2)−O(11) 66.39(26), Pb(2)−O(11)−Pb(1) 110.50(32), Pb(2)−O(2)−Pb(1) 106.54(32), Pb(1)−O(1)−Pb(1′) 114.85(33). The non-hydrogen atoms are shown as the 30% probability ellipsoids. The Pb−O distances with nitrate bridging ions are marked with dotted lines.

the sum of van der Waals radii (3.44 Å).[32] With regard to quite long $\mathrm{Pb{-}O_{(ClO4)}}$ distances, compound **2** can be described as an ionic structure built up from tropolonato−lead chains with positive charge on the Pb(2) atoms neutralized by negatively charged parallel rows of $\mathrm{ClO_4^-}$ ions. The charge on the Pb(1) atoms is neutralized due to chelation by two tropolonate anions.

The presence of distinct empty volumes around the Pb(1) and Pb(2) atoms shows that the $6s^2$ lone electron pair on both lead(II) ions is stereochemically active. In the arrangement around the lead(II) ions, four adjacent shorter and four longer Pb−O distances are seen. The observed pattern with 4 + 4 coordination has been attributed by some authors to indicate a stereochemically active lone $6s^2$ electron pair.[35]

$[\mathrm{Pb_2(trop)_2(NO_3)_2(CH_3OH)}]_n$ (3). Compound **3** has a polymeric structure with the $[\mathrm{Pb_2(trop)_2(NO_3)_2(CH_3OH)}]$ fragment repeated in the polymeric chain (Figure 4). Two types of lead(II) ions, Pb(1) and Pb(2), both with coordination number seven, are present in **3**. Both lead(II) ions are chelated by one tropolonato ligand resulting in Pb−O bond lengths of 2.317(9) and 2.346(9) Å, and 2.350(9) and 2.361(9) Å for the Pb(1) and Pb(2) ions, respectively. The tropolonato ligand bound to Pb(1) also forms two bridges to neighboring lead(II) ions with Pb−O distances of 2.597(8) and 2.769(8) Å, while the same ligand chelated to Pb(2) builds only one such a bridge with the Pb−O distance of 2.758(8) Å. Thus, in compound **3**, the tropolonato ligand behaves either as a dimetallic triconnective or as a trimetallic tetraconnective bridge. In addition, the Pb(1) ion is chelated by one $\mathrm{NO_3^-}$ ion (Pb−O bond lengths 2.672(9) and 2.821(11) Å), while the Pb(2) ion is chelated by two such ions. From this, of the two nitrate ions, one is bonded to the Pb(2) ion more strongly than the other, as is shown by the respective pairs of Pb−O distances: 2.569(11) and 2.805(10) Å for the first, and 2.868(10) and 3.010(9) Å for the second $\mathrm{NO_3^-}$ ion. A very wide range of Pb−O distances is found in lead(II) complexes with the nitrate ion in the inner coordination sphere. The shortest observed $\mathrm{Pb{-}O_{(NO3)}}$ bond distances are equal to 2.43, 2.45,[44] and 2.49 Å.[45]

Two types of nitrate anions are observed in structure **3**. The first type is both bidently chelating and with one of its oxygen atoms bridging two different lead atoms. These $\mathrm{NO_3^-}$ bridges between two lead(II) ions (Pb(1) and Pb(2)) form two four-membered rings and consequently link two $[\mathrm{Pb_2(trop)_2(CH_3OH)}]$ units together. The second type of $\mathrm{NO_3^-}$ ions behaves only as a chelating agent toward the Pb(2) ions. There are numerous crystal structures in which nitrate groups coordinate lead(II) ions in monodentate, bidently chelating, and bridging fashion. The same type of bridge (μ_2-nitrato-*O,O,O′,O″*) as in structure **3** was also found in a few lead(II) complexes reported previously.[46]

Another difference in the coordination of the two lead(II) ions in structure **3** is that only the Pb(1) ion coordinates a methanol molecule. The $\mathrm{Pb{-}O_{(MeOH)}}$ bond distance is 2.559(10) Å. A limited number of crystal structures with methanol coordinated to a lead(II) ion is reported with $\mathrm{Pb{-}O_{(MeOH)}}$ bond distances of 2.45,[47] 2.53,[48] and 2.65 Å.[49] The large empty space in the coordination sphere around the lead(II) ions in this compound shows that the lone $6s^2$ electron pair is stereochemically active.

The chains of **3** form contacts between lead(II) ions and oxygen atoms from a neighboring chain with distances of 3.068(10) and 3.390(16) Å giving rise to sheets from which the tropolonato rings protrude (Figure 5).

$[\mathrm{Pb(trop)_2}]_2$ (4). The crystal structure of $\mathrm{Pb(trop)_2}$, shown in Figure 6, consists of dimeric $[\mathrm{Pb(trop)_2}]_2$ units. Two $[\mathrm{Pb(trop)_2}]$ entities are held together by rather long bridging Pb−O interactions, 2.889(11) Å. This behavior of lead(II) is different from that of its lighter congener in group 14, tin(II), which forms a monomeric complex, $[\mathrm{Sn(trop)_2}]$.[2] Dimeric structures similar to **4** were found in a few other lead(II) complexes where both bidentate *O*-donor ligands are chelating, and one of them also bridging.[50]

---

(44) Rutsch, P.; Huttner, G. *Angew. Chem., Int. Ed.* **2000**, *39*, 2118−2120.

(45) Bashall, A.; McPartlin, M.; Murphy, B. P.; Fenton, D. E.; Kitchen, S. J.; Tasker, P. A. *J. Chem. Soc., Dalton Trans.* **1990**, 505−509.

(46) (a) Harrowfield, J. M.; Miyamae, H.; Skelton, B. W.; Soudi, A. A.; White, A. H. *Aust. J. Chem.* **1996**, *49*, 1029−1042, 1081−1088. (b) Boudaren, C.; Auffredic, J.-P.; Benard-Rocherulle, P.; Louer, D. *Solid State Sci.* **2001**, *3*, 847−858. (c) Nordell, K. J.; Schultz, K. N.; Higgins, K. A.; Smith, M. D. *Polyhedron* **2004**, *23*, 2161−2167. (d) Morsali, A; Mahjoub, A. R. *Chem. Lett.* **2004**, *33*, 64−65.

(47) Parr, J.; Ross, A. T.; Slawin, A. M. Z. *Polyhedron* **1997**, *16*, 2765−2770.

(48) Bashall, A.; McPartlin, M.; Murphy, B. P.; Powell, H. R.; Waikar, S. *J. Chem. Soc., Dalton Trans.* **1994**, 1383−1390.

(49) Hou, H.; Li, L.; Li, G.; Fan, Y.; Zhu, Y. *Inorg. Chem.* **2003**, *42*, 3501−3508.

(50) (a) Chandler, C. D.; Hampden-Smith, M. J.; Deusler, E. N. *Inorg. Chem.* **1992**, *31*, 4891−4893. (b) Uzoukwu, B. A.; Adiukwu, P. U.; Al-Juaid, S. S.; Hitchcock, P. B.; Smith, J. D. *Inorg. Chim. Acta* **1996**, *250*, 173−176. (c) Malik, M. A.; O'Brien, P.; Motevali, M.; Jones, A. C.; Leedham, T. *Polyhedron* **1999**, *18*, 1641−1646. (d) Ahmed, S. I.; Burgess, J.; Fawcett, J.; Parsons, S. A.; Russell, D. R.; Laurie, S. H. *Polyhedron* **2000**, *19*, 129−135. (e) Harrowfield, J. M.; Maghaminia, S.; Soudi, A. A. *Inorg. Chem.* **2004**, *43*, 1810−1812. (f) Pettinari, C.; Marchetti, F.; Pettinari, R.; Cingolani, A.; Rivarola, E.; Phillips, C.; Tanski, J.; Rossi, M.; Caruso, F. *Eur. J. Inorg. Chem.* **2004**, 3484−3497.

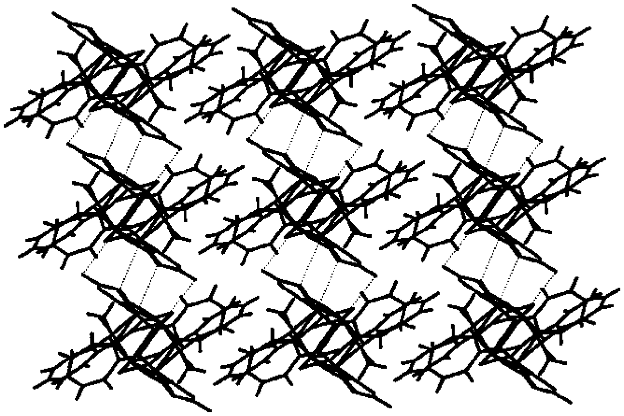

Figure 5. Wireframe view of crystal structure **3** with marked Pb···$O_{(NO3)}$ distances (dotted lines) between chains.

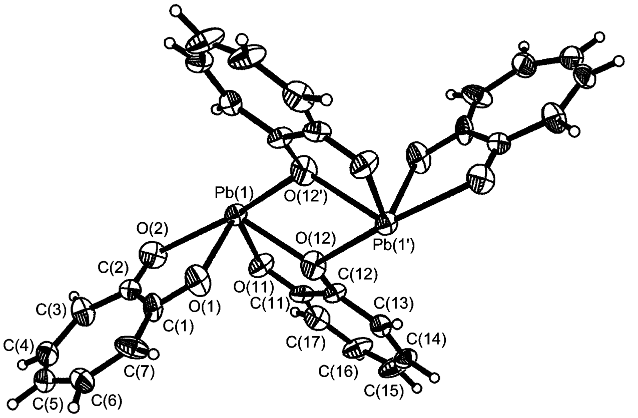

Figure 6. Molecular structure of **4**. Selected bond lengths (Å), distances (Å), and angles (deg) are as follows: Pb(1)−O(1) 2.335(14), Pb(1)−O(2) 2.389(14), Pb(1)−O(11) 2.298(13), Pb(1)−O(12) 2.375(13), Pb(1)−O(12′) 2.889(11), Pb(1)···Pb(1′) 4.414(1), O(1)−Pb(1)−O(2) 67.45(44), O(11)−Pb(1)−O(12) 66.82(39), O(1)−Pb(1)−O(11) 102.04(61), O(2)−Pb(1)−O(12) 124.31(49), O(1)−Pb(1)−O(12) 80.91(49), O(2)−Pb(1)−O(11) 76.26(54), C(2)−O(2)−Pb(1) 118.53(1.10), C(1)−O(1)−Pb(1) 118.59(1.15), C(12)−O(12)−Pb(1) 118.61(1.03), C(11)−O(11)−Pb(1) 121.64(1.10), Pb(1)−O(12)−Pb(1′) 113.64(46). The non-hydrogen atoms are shown as the 30% probability ellipsoids.

Both tropolonato ligands in **4** adopt a "V" shape in respect to the presence of the stereochemically active $6s^2$ lone electron pair on the lead(II) ion, which is located on the opposite side of the ligand rings. The bite angles in **4** are 67.45(44)° and 66.82(39)° and the angles within the $Pb_2(\mu\text{-}O)_2$ plane are 66.36(46)° and 113.64(46)°. With the tropolonato ligand acting simultaneously as chelating and bridging agent, the Pb−O bond distances are 2.298(13) and 2.375(13) Å. For the only chelating tropolonato ligand, somewhat longer metal−oxygen contacts are observed, 2.335(14) and 2.389(14) Å.

The coordination polyhedron of **4**, formed by four chelating O atoms and the stereochemically active lone $6s^2$ electron pair, is a distorted square pyramid with the electron pair located in the apex. If the Pb−O bridging distance is taken into account, then the geometry around lead(II) ion can be described as a capped distorted square pyramid or a distorted trigonal prism with one apex position occupied by the lone pair.

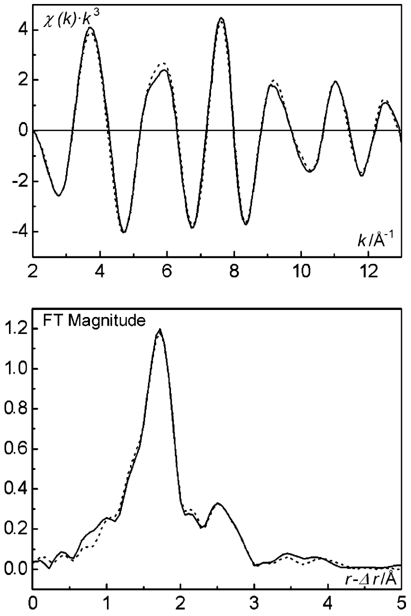

Figure 7. (Top) EXAFS k^3-weighted experimental lead L_{III}-edge data and (bottom) Fourier transformed EXAFS data of solid $Pb(trop)_4$ compound (—) with fitted model functions (---).

Structure of $Pb(trop)_4$ (5). This structure was determined by means of EXAFS, as it was not possible to obtain single crystals suitable for a crystallographic examination. The EXAFS data reveal a mean Pb−O bond distance of 2.251(2) Å. This bond distance indicates an eight-coordinated complex. The fairly small Debye−Waller factor coefficient, $\sigma^2 = 0.0061(2)$ Å^2, shows a narrow bond distance distribution for this coordination number. The weak multiple scattering is in coherence with a low symmetry around the lead(IV) ion. The fit of the experimental data and the Fourier transform are shown in Figure 7.

Only two complexes in which lead(IV) coordinates eight oxygen atoms (four bidentate ligands) have been structurally characterized; tetrakis(acetato)lead(IV)[51] and tetrakis(*o*-benzoylbenzoato)lead(IV).[52] These complexes have the mean Pb−O bond length of 2.27 Å, similar to that observed in **5**. The Pb−O bond distances in four- and six-coordinated lead(IV) compounds are significantly shorter, in the range 2.05−2.08 Å for the $[PbO_4]^{4-}$ ion,[53] and 2.15−2.17 Å for the $[Pb(IO_6)_6]^{2-}$ and $[Pb(OH)_6]^{2-}$ ions.[54]

IR Spectroscopy. Infrared spectra of the solid complexes and the vibrational frequencies with proposed assignments are collected in the Supporting Information. The bands observed can be divided into three groups: the internal vibration of tropolonate moiety, the anion (trifluoromethanesulfonate, perchlorate, or nitrate), and the metal−

---

(51) Prout, K.; Vaughan-Lee, D.; Moloney, M. G.; Prottey, S. C. *Acta Crystallogr., Sect. C* **1996**, *52*, 351−354.

(52) Schurmann, M.; Huber, F. *Acta Crystallogr., Sect. C* **1994**, *50*, 1710−1713.

(53) (a) Martens, K. P.; Hoppe, R. *Z. Anorg. Allg. Chem.* **1977**, *437*, 105−115. (b) Stoll, H.; Hoppe, R. *Z. Anorg. Allg. Chem.* **1984**, *39*, 566−576. (c) Brandes, R.; Hoppe, R. *Z. Anorg. Allg. Chem.* **1994**, *620*, 1346−1350.

(54) (a) Zloczysti, S.; Hartl, H.; Frydrych, R. *Acta Crystallogr., Sect. B* **1976**, *32*, 753−758. (b) Levy-Clement, C.; Billiet, Y. *Bull. Soc. Fr. Mineral. Cristallogr.* **1978**, *34*, 361−372. (c) Jacobs, H.; Stahl, R. *Z. Anorg. Allg. Chem.* **2000**, *626*, 1863−1866.

ligand bonds. The vibrational spectra of tropolonato−lead complexes are quite complicated; therefore, interpretations were based on previous assignments of characteristic frequencies. A full assignment of bands on the basis of normal coordinate analyses in combination with experiments and quantum chemical calculations has been performed for the uncoordinated tropolone.[55] The IR spectra of a series of tropolonato−metal(II) and −metal(III) complexes have been presented in detail.[56] Some efforts to describe the main bands for bismuth(III), gallium(III), and indium(III) complexes have been made.[4,11]

The bands belonging to the tropolonato ligand dominate the spectra. The functional groups of tropolone (hydroxyl and carbonyl) form bonds with lead(II) ions. This is confirmed by the lack of distinct vibrations around 3200, 1267, and 757 cm^{-1} originating from the stretching, bending, and torsional modes of the OH group in uncoordinated tropolone.[55] In addition, the partial loss of the C═O double bond character after complexation of the tropolone to the lead(II) ion is shown by the shift of the ν(C═O) bands to lower wavenumbers, from 1613 and 1548 cm^{-1} in free ligand[56] to about 1592 and 1503 cm^{-1} in complexes. Instead of closely lying (almost overlapping) quite broad absorption bands in the region 1620−1400 cm^{-1} in free tropolone, four distinct narrow and well separated bands at approximately 1590, 1500, 1420, and 1350 cm^{-1} have been observed in the studied complexes.

The main bands derived from vibrations of the $CF_3SO_3^-$, ClO_4^-, and NO_3^- ions are located in the middle part of the infrared spectrum just as for other complexes containing these anions.[57]

The Pb−O stretching frequencies in tropolonato−lead(II) systems are found in the far-infrared region at 495 and 517 for **1**, 492 and 522 for **2**, 504 and 518 for **3**, and 497 and 513 cm^{-1} for **4**. The bands belonging to Pb^{IV}−O stretching vibrations in **5** are broader and occur at 493 and 534 cm^{-1}. The lead(II)−oxygen vibrations appear at frequencies similar to those observed for the Pb−O bands at 500 and 530 or 500, 508, and 538 cm^{-1} in lead(II) edta complexes.[58] This type of band was also found at 467, 474, or 476 cm^{-1} in bis(β-diketonato)lead(II) complexes.[50c] The O−Pb−O bending vibrations in the studied tropolonato−lead systems can possibly be assigned to bands below 240 cm^{-1}.

Conclusions and Summary

The reaction of Htrop with $Pb(CF_3SO_3)_2$, $Pb(ClO_4)_2$, and $Pb(NO_3)_2$ in water/methanol mixtures produced a new series of compounds, provided the pH of the reaction mixture was below 1. The X-ray crystal structure determinations, reported here, revealed curious types of polymeric compounds with chain (**1** and **3**) or net structures (**2**). When the pH of the reaction mixture is above 2 then, independently of the counterion used, dimeric $[Pb(trop)_2]_2$ (**4**) is formed. The reported lead(II) compounds display different total coordination numbers of the lead(II) ion, from five in $[Pb(trop)_2]_2$, to seven in $[Pb(trop)(CF_3SO_3)(H_2O)]_n$ and $[Pb_2(trop)_2(NO_3)_2(CH_3OH)]_n$, to eight in $[Pb_3(trop)_4(ClO_4)_2]_n$.

The type of compound formed depends on the pH of the solution. The polymeric compounds were only formed in solutions with very low pH. This low pH, <1, prevents the formation of compound **4** or causes the transfer of **4** into a polymeric compound (see Experimental Section, the preparation of **2**). At higher pH, only the dimeric compound **4** is formed, regardless of the lead(II) salt used. An increase of pH of the aqueous−methanolic reaction mixtures of lead(II) triflate, perchlorate, or nitrate and tropolone, by addition of, e.g., sodium hydroxide solution, also leads to the formation and precipitation of **4**. This shows that these systems are completely reversible, and the composition of the product is determined by pH and the presence of suitable anions. The lead(II) ion binds very easily one tropolone molecule in solution. The dislodgement of a proton from the second Htrop molecule by the $Pb(trop)^+$ moiety is more difficult in solutions at pH < 1 but takes place at higher pH. Very low pH impedes the formation of the $Pb(trop)_2$ moiety and favors the polymerization process. It is clearly seen that under such conditions the $CF_3SO_3^-$, ClO_4^-, and NO_3^- ions, which are weakly coordinating ligands, can enter (or approach) the coordination sphere of the lead(II) ion during crystallization. Thus, our results also show that the counteranions play a decisive role in the formation of the polymeric compounds. In compounds **1** and **3**, the counteranions build bridges within the same polymeric chain, whereas in compound **2** they link two adjacent polymeric chains forming a three-dimensional network. Moreover, in **3** the NO_3^- ions connect chains into sheets. Undoubtedly, the formation of respective polymeric compounds depends on the geometry of the counteranion and the number of its accessible oxygen donor atoms. A comparison of the respective Pb−O bond distances shows that perchlorate ions interact with metal atoms more weakly than the triflate and nitrate groups. Because of quite long $Pb-O_{(ClO4)}$ distances (>3.0 Å), structure **2** can be also regarded as an ionic compound with the formula $[Pb_3(trop)_4](ClO_4)_2$.

The nonspherical distribution of ligands surrounding the lead(II) ion (hemidirected geometry)[35] in the structures **1**, **3**, and **4** results from the presence of the stereochemically active $6s^2$ lone electron pair. In compound **2**, a hemidirected geometry can be considered if only the tropolonato ligands are taken into account. The gap observed in this complex is filled, apart from the lone electron pair, with the weakly bonding ClO_4^- ions. The $6s^2$ lone electron pair on the lead(II) ions is stereochemically active in all the studied complexes. The active lone electron pair is common in lead-

---

(55) Rostkowska, H.; Lapinski, L.; Nowak, M. J.; Adamowicz, L. *Int. J. Quantum Chem.* **2002**, *90*, 1163−1173.

(56) Burden, K. J.; Thornton, D. A.; Watkins, G. M. *Spectrochim. Acta* **1989**, *45A*, 1179−1186.

(57) (a) Nakamoto, K. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 4th ed.; Wiley-Interscience: New York, 1986; Part III-11. (b) Molla-Abbassi, A.; Eriksson, L.; Mink, J.; Persson, I.; Sandström, M.; Skripkin, M.; Ullström, A.; Lindqvist-Reis, P. *J. Chem. Soc., Dalton Trans.* **2002**, 4357−4364.

(58) McConnell, A. A.; Nuttall, R. H. *Spectrochim. Acta* **1977**, *33A*, 459−462.

(II) complexes with coordination number up to eight, but it does not occur for higher coordination numbers.[35]

The structure of solid Pb(trop)$_4$ (**5**), studied by means of the EXAFS technique, revealed coordination number eight for lead(IV) ion with a mean Pb−O bond distance of 2.251(2) Å.

Acknowledgment. The authors gratefully acknowledge the Stanford Synchrotron Radiation Laboratory (SSRL) for allocation of beam time and placement of laboratory facilities at our disposal during EXAFS measurements. SSRL is operated by the Department of Energy, Office of Basic Energy Sciences. The SSRL Biotechnology Program is supported by the National Institutes of Health, National Center for Research Resources, Biomedical Technology Program, and by the Department of Energy, Office of Biological and Environmental Research. We thank Professor Slawomir Siekierski, Institute of Nuclear Chemistry and Technology, for helpful discussions and Dr. Corine Sandström, Swedish University of Agricultural Sciences, for help with the NMR measurements.

Supporting Information Available: Crystallographic data in CIF format for **1**−**4**, IR frequencies with proposed assignements (Table S1), mid- and far-IR spectra (Figures S1−S5). This material is available free of charge via the Internet at http://pubs.acs.org.

IC061561F