are essentially identical, except that for the bromide analogue, we find a broad, medium-intensity band at ca. 520 cm^{-1} which we assign to ν(Cu–O). No band down to energies of 200 cm^{-1} was found which could be assigned to the ν(Cu–Br) frequency. Its apparent shift to lower energy is consistent with vibrational differences between metal–chloride and metal–bromide bonds.

The general characteristics of Cu_4OCl_6(3-quin)$_4$·$0.75CH_3C_6H_5$ compare with those found for other such systems: $CuCl_5^{3-}$ [22,26] and several tetramers.[1-17]

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Registry No. Cu_4OCl_6(3-quin)$_4$, 62237-84-7.

Supplementary Material Available: Listing of structure factor amplitudes (22 pages). Ordering information is given on any current masthead page.

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Heavy-Metal Complexes of 2,4,6-Tris(2-pyrimidyl)-1,3,5-triazine. Structure of a Dilead Derivative

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The syntheses of four heavy-metal complexes of the ligand 2,4,6-tris(2-pyrimidyl)-1,3,5-triazine (TPymT) are reported. One of the complexes, 2,4,6-tris(2-pyrimidyl)-1,3,5-triazinedioxouranium(VI) nitrate heptahydrate, contains only one heavy-metal atom per ligand while the other three, bis[2,4,6-tris(2-pyrimidyl)-1,3,5-triazine]heptathallium(I) nitrate, 2,4,6-tris(2-pyrimidyl)-1,3,5-triazinetrilead(II) chloride trihydrate, and 2,4,6-tris(2-pyrimidyl)-1,3,5-triazinedilead(II) nitrate dihydrate, have more than one metal atom per ligand. The dilead complex crystallizes from aqueous solution as the dihydrate salt having the composition $C_{15}N_9H_9Pb_2(NO_3)_4{\cdot}2H_2O$. The structure of this complex has been determined in a single-crystal x-ray diffraction study. The pale yellow complex crystallizes in the monoclinic space group $P2_1/n$ with four formula units per unit cell. The lattice parameters are $a = 14.192$ (2) Å, $b = 9.240$ (2) Å, $c = 19.621$ (3) Å, and $\beta = 90.173$ (6)°. By using 3184 independent observed reflections collected by diffractometer, the structure was solved and refined to a final discrepancy factor, R_1, of 0.044. The structure is twinned on the (100) plane. The proportion of each component of the twinned lattice was determined in the least-squares refinement. The twinning parameter refined to 0.160 (1) indicating the proportions of the two lattices to be 84:16. The triazine ligand binds two crystallographically unique lead atoms in two of its three tridentate sites. These lead atoms are bridged by the nitrate anion and water molecule oxygen atoms to form a polymer along the crystallographic b axis. The ring system of the 2,4,6-tris(2-pyrimidyl)-1,3,5-triazine ligand is puckered and a water molecule is hydrogen bonded in the third, terpyridine-like site. Conductivity data show the two lead atoms to remain coordinated to the TPymT ligand in aqueous solution.

Introduction

Interest in metals as probes of biological structure and function has grown during the last two decades. Metals have been used extensively as isomorphous replacement reagents for determining the phases of scattered x rays in crystal structures of macromolecules,[1] for probing the many parameters involved in the intercalative binding of drugs to deoxyribonucleic acid, DNA,[2-6] and for assessing site ac-

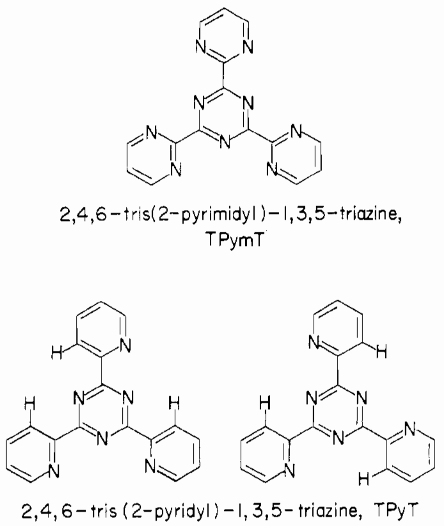


Figure 1. Structures of the ligands 2,4,6-tris(2-pyrimidyl)-1,3,5-triazine (top) and 2,4,6-tris(2-pyridyl)-1,3,5-triazine (bottom).

cessibility of specific regions of transfer ribonucleic acids, tRNA,[7-11] and they have been used as stains for viewing structure in electron micrographs.[12-23]

Recent studies[24] in our laboratory have demonstrated that phosphorothioate $[(RO)_2P(S)O]^-$ groups, incorporated into specific sites on the sugar–phosphate backbone of enzymatically synthesized[25] nucleic acid polymers, react selectively and quantitatively with platinum reagents. The presence of the class b (or soft)[26] sulfur ligands in a polynucleotide offers the possibility of attaching polymetallic electron-dense reagents at these sites for use in electron microscopy. Although single heavy-metal atoms have been visualized in electron micrographs,[20,23] polymetallic stains would greatly enhance the image contrast.

The present study was initiated as a first attempt to provide water-soluble, polymetallic heavy-atom reagents that would bind sulfur in a biopolymer. The ligand employed was 2,4,6-tris(2-pyrimidyl)-1,3,5-triazine, TPymT (Figure 1). This molecule and the chemically similar 2,4,6-tris(2-pyridyl)-1,3,5-triazine, TPyT (Figure 1), were first synthesized in 1959.[27] The latter compound has been studied extensively as an analytical reagent for iron,[28-31] cobalt,[32] and ruthenium[33] and as a ligand that could bind two metals in terpyridine- and bipyridine-like sites or three metals in bipyridine-like binding sites.[34-39] To our knowledge, however, no stable crystalline complex of TPyT with more than one metal ion has been reported. This result is not surprising since the protons on the C-6 carbon atoms of the pyridyl rings would be expected to block metal coordination in all but the terpyridine-like site (Figure 1). TPymT offers the possibility of binding three metals in tridentate, terpyridine-like sites. It has, however, received little attention from coordination chemists, perhaps because of the reported low yield and length of time involved in its synthesis.[40]

In this paper we describe the preparation of several heavy-metal complexes of TPymT. Three of the complexes of TPymT that we report contain more than one metal per ligand molecule. The structure of one derivative, $(TPymT)Pb_2(NO_3)_4\cdot 2H_2O$, is described. The accompanying paper[41] reports details of the copper-promoted hydrolysis of the TPymT ligand and the crystal structure of the product. A preliminary communication describing some of these results and an improved synthesis of TPymT has appeared.[42]

Experimental Section

Preparation of Compounds. All chemicals were of reagent grade quality and used without further purification. Chemical microanalyses were performed by Galbraith Laboratories, Knoxville, Tenn.

2,4,6-Tris(2-pyrimidyl)-1,3,5-triazine. The synthesis of this compound was reported previously.[42] Its complete IR and mass spectral bands are as follows. **IR** (Nujol mull): 3060 (w), 1568 (m), 1536 (s), 1445 (s), 1430 (m), 1278 (w), 1217 (m), 1182 (w), 994 (m), 862 (w), 848 (m), 825 (m), 786 (m), 720 (w), 680 (s), 633 (w) cm^{-1}. **MS**: m/e 315 (parent ion, 58), 316 (11), 210 (3), 209 (3), 157.5 (1), 131 (7), 107 (4), 106 (51), 105 (100), 95 (4), 79 (21), 78 (21), 53 (21), 52 (11).

$(TPymT)UO_2(NO_3)_2\cdot 7H_2O$. TPymT, 0.100 g (0.32 mmol), was shaken in water with 0.475 g (0.95 mmol) of uranyl nitrate, $UO_2(NO_3)_2\cdot 6H_2O$. The resulting yellow solution was allowed to stand overnight whereupon crystals formed. The crystals were collected and washed with water. The infrared spectrum (KBr) showed the ligand modes and the presence of uranyl and nitrate ions. Anal. Calcd for $C_{15}N_{11}H_{23}O_{15}U$: C, 21.56; H, 2.78; N, 18.44. Found: C, 21.48; H, 2.62; N, 18.33. **IR** (KBr pellet): 3280 (m), 2985 (m), 1585 (w), 1527 (s), 1424 (w), 1376 (s), 1362 (s), 1095 (w), 1045 (w), 1024 (w), 1012 (w), 946 (s), 862 (w), 806 (w), 780 (m), 692 (s) cm^{-1}.

$(TPymT)Pb_3Cl_6\cdot 3H_2O$. A 0.052-g (0.167-mmol) sample of TPymT was heated in water with 0.139 g (0.50 mmol) of anhydrous $PbCl_2$ until all of the reactants dissolved. The resulting bright yellow solution was cooled yielding 0.133 g (67%) of a bright yellow powder. Attempts to grow crystals suitable for x-ray diffraction studies were unsuccessful. Anal. Calcd for $C_{15}N_9H_{15}O_3Pb_3Cl_6$: C, 14.97; H, 1.26; N, 10.48; Cl, 17.67. Found: C, 14.40; H, 1.25; N, 10.41; Cl, 17.47. **IR** (Nujol mull): 1570 (w), 1533 (s), 1280 (w), 1095 (w), 1003 (m), 961 (w), 850 (w), 833 (w), 815 (m), 763 (s), 715 (m), 684 (s), 630 (w) cm^{-1}.

$(TPymT)Pb_2(NO_3)_4\cdot 2H_2O$. A 0.165-g (0.5-mmol) aqueous solution of $Pb(NO_3)_2$ was heated with 0.052 g (0.167 mmol) of TPymT. The resulting pale yellow solution yielded a pale yellow microcrystalline product which could be recrystallized from water to yield large needle crystals. The microcrystalline powder was dried over P_2O_5 in vacuo and sent for analysis. Anal. Calcd for $C_{15}N_{13}H_{11}O_{13}Pb_2$, a monohydrate: C, 18.09; H, 1.12; N, 18.29. Found: C, 17.96; H, 0.90; N, 18.31. **IR** (Nujol mull): 3095 (w), 1583 (w), 1555 (s), 1538 (sh), 1320 (s), 1273 (s), 1198 (w), 1160 (w), 1130 (w), 1112 (w), 1038 (w), 1025 (m), 1013 (m), 1005 (m), 873 (m), 836 (w), 818 (s), 775 (s), 725 (s), 720 (sh), 693 (s), 653 (m) cm^{-1}. Subsequent x-ray structure analysis determined that the crystals were in fact a dihydrate (vide infra).

$(TPymT)_2Tl_7(NO_3)_7$. A 0.133-g (0.5-mmol) water solution of $TlNO_3$ was boiled with 0.052 g (0.167 mmol) of TPymT. The dark yellow solution was allowed to evaporate to yield dark yellow platelike crystals. Anal. Calcd for $C_{30}N_{25}H_{18}O_{21}Tl_7$: C, 14.43; H, 0.72; N, 14.04. Found: C, 14.95; H, 0.68; N, 14.26. **IR** (Nujol mull): 1582 (w), 1532 (s), 1345 (s), 1310 (s), 1280 (s), 1038 (w), 1000 (m), 862 (w), 820 (m), 778 (m), 723 (m), 690 (m), 635 (w) cm^{-1}.

Conductivity Studies on $(TPymT)Pb_2(NO_3)_4\cdot 2H_2O$. Solutions of $(TPymT)Pb_2(NO_3)_4\cdot 2H_2O$ were prepared by dissolving the complex in hot, distilled, deionized water, allowing the solutions to cool, and then diluting to the mark in volumetric glassware. To minimize errors at least 15 mg of the material was weighed out for each solution and no solutions were made by serial dilution. The conductivity of each of the samples, which had $0.01 < (\text{equivalent concentration})^{1/2} < 0.07$, was measured at 25 °C using a conductivity cell calibrated with 0.01 M KCl and a Beckman RC-18A conductivity bridge. The values were corrected for background conductance of water.

Physical Measurements. Infrared spectra were obtained with Perkin-Elmer 137 and 621 spectrophotometers and calibrated with polystyrene. Mass spectra were obtained on a JEOL JMS-07 EI mass spectrometer.

Structure Determination of $(TPymT)Pb_2(NO_3)_4\cdot 2H_2O$

Collection and Reduction of the X-Ray Data. The crystals used for x-ray studies were cut from large needle crystals grown by slow evaporation of an aqueous solution of the compound. A crystal of $(TPymT)Pb_2(NO_3)_4\cdot 2H_2O$ was mounted along the needle axis and investigated by Weissenberg and precession photographic methods. The crystal was found to belong to the monoclinic system. The observed extinctions of $h0l$, $h + l \neq 2n$, and $0k0$, $k \neq 2n$, uniquely determined the space group to be $P2_1/n$, a nonstandard setting of $P2_1/c$ that was retained because of its more nearly orthogonal β angle.

Intensity data were collected on a crystal of dimensions 0.08 × 0.17 × 0.23 mm along the a, b, and c crystallographic axes, respectively, which was intentionally offset from the b^* axis by approximately 2°.

Table I. Experimental Details of the X-Ray Diffraction Study of (TPymT)$Pb_2(NO_3)_4 \cdot 2H_2O$

(A) Crystal Parameters[a] at 23 °C

$a = 14.192$ (2) Å	Mol wt 1013.8
$b = 9.240$ (2) Å	Space group $P2_1/n$
$c = 19.621$ (3) Å	$Z = 4$
$\beta = 90.173$ (6)°	ρ(calcd) = 2.617 g/cm^3
$V = 2573.1$ Å^3	ρ(obsd)[b] = 2.609 (3) g/cm^3

(B) Measurement of Intensity Data

Instrument: Picker FACS-I-DOS diffractometer

Radiation: Mo Kα (λ_{α_1} 0.7093 Å), graphite monochromatized

Takeoff angle: 1.82°

Detector aperature: 6.33 × 6.33 mm

Crystal–detector distance: 33 cm

Scan technique: coupled θ(crystal)–2θ(counter)

Scan range: 1.75° (symmetric, plus Kα_1–Kα_2 dispersion)

Scan rate: 1.0°/min

Maximum 2θ: 55°

Background measurements: stationary crystal, stationary counter; 20-s counts at each end of 2θ scan range

Standards: three reflections [$(\bar{4}08)$, (229), (042)] measured after every 47 data reflections

Final intensities of standards: 97.7, 93.2, and 91.5% of their respective initial values; corrections applied to data (see below)

No. of reflections collected: 6872 [$2\theta \leqslant 20°$ ($\pm h, +k, \pm l$), $20 < 2\theta < 55°$ ($\pm h, +k, +l$)]; 5935 unique, non space group extinguished

(C) Treatment of Intensity Data[c]

Reduction to preliminary F_o^2 and $\sigma(F_o^2)$: correction for background, attenuators, and Lorentz–polarization effects of monochromatized x radiation in the usual manner,[d] $\epsilon^f = 0.04$; Picker scalar truncation handled by adding 0.45 to each counted value and multiplying by 10; extra term of 24.75 added to $\sigma^2(I)$ to account for the errors in this roundoff[g]

Correction for crystal decomposition:[h] data scaled for anisotropic decay of crystal

$$(\text{scale})_j = 1.0 \Bigg/ \left[(P_{1j}^2 + P_{2j}^2 + P_{3j}^2) \Bigg/ \left(\frac{P_{1j}^2}{K_{1j}^2} + \frac{P_{2j}^2}{K_{2j}^2} + \frac{P_{3j}^2}{K_{3j}^2} \right) \right]^{1/2}$$

where K_{ij} = fraction of intensity remaining for the ith standard at the time of collecting jth reflection and P_{ij} = cosine of the angle between the reciprocal lattice vectors of the ith standard and jth reflection

Absorption correction: $\mu = 132.5$ cm^{-1}; transmission factors varied between 0.08 and 0.37

Averaging: done over two equivalent forms, $R_{av}{}^i = 0.019$

Scaling: Wilson's method[j]

Observed data: 3184 unique reflections for which $F_o^2 > 3\sigma(F_o^2)$

[a] From a least-squares fit to the setting angles of 25 reflections having $2\theta > 30°$. [b] By flotation in mixtures of bromoform and carbon tetrachloride. [c] Programs for an IBM 360-91 computer used in this work: UMAT, the local version of the Brookhaven diffractometer setting and cell constant and orientation refinement program; ORABS, the local version of the absorption correction program by D. J. Wehe, W. R. Busing, and H. S. Levy modified for the Picker FACS-I geometry; further modified by E. I. Lerner to calculate the Zachariasen beta function[43] modified for the Picker FACS-I geometry[44]

$$\beta(2\theta) = \frac{(1 + \cos^2 2\theta_m)(\cos^2 2\theta_m + \cos^4 2\theta)(\mathrm{d}A^{-1}/\mathrm{d}\mu)_{2\theta}}{(\cos^2 2\theta_m + \cos^2 2\theta)^2 (\mathrm{d}A^{-1}/\mathrm{d}\mu)_{\theta=0}}$$

where A is the transmission factor; XDATA, the Brookhaven Wilson plot and scaling program; FORDAP, the Zalkin Fourier program; CUGLS, the local version of the Busing–Martin–Levy structure factor calculation and least-squares refinement program (ORFLS) modified by Ibers and Doedens for rigid-body refinement and further modified by E. I. Lerner for this twinned structure (see text); ORFFE, the Busing–Martin–Levy molecular geometry and error function program; TRACER II, the Lawton lattice transformation–cell reduction program; ORTEP, the Johnson thermal ellipsoid plotting program; in addition, various local data-processing programs. [d] B. G. Segal and S. J. Lippard, *Inorg. Chem.*, **13**, 822 (1974); $(Lp)^{-1} = (1 + \cos^2 2\theta_m)(\sin 2\theta)/(\cos^2 2\theta_m + \cos^2 2\theta)$ (see footnote *e*). [e] L. V. Azaroff, *Acta Crystallogr.*, 8, 701 (1955). [f] P. W. R. Corfield, R. J. Doedens, and J. A. Ibers, *Inorg. Chem.*, **6**, 197 (1967). [g] M. R. Churchill and B. G. DeBoer, *ibid.*, **12**, 525 (1973):

$$\sigma^2(I) = 10(\text{Cts} + 0.45) + \left[(t_c/2t_b)\right]^2 [10(B_1 + B_2 + 0.9)] + 24.75 + \epsilon^2 I^2$$

[h] M. R. Churchill and K. L. Kalra, *ibid.*, **13**, 1427 (1974), footnote 12. [i] $R_{av} = \Sigma^N |F^2(\text{av}) - F^2| / \Sigma^N F^2$; N is the number of reflections measured more than once. [j] A. J. C. Wilson, *Nature (London)*, **150**, 151 (1942).

The mosaicity of the crystal was surveyed by ω and 2θ scans on several strong, low-angle reflections with a wide open counter. The mosaic spread was found to be acceptable with the width at half-height of the ω scans ranging from 0.11 to 0.15°. Details of the data collection and reduction are given in Table I.

Solution and Refinement of the Structure. The positions of the two crystallographically independent lead atoms were determined from an unsharpened three-dimensional Patterson map. Least-squares refinement of the overall scale factor, atomic positional parameters, and lead atom isotropic temperature factors reduced the discrepancy factors $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_2 = (\sum w(|F_o| - |F_c|)^2/\sum wF_o^2)^{1/2}$ to 0.200 and 0.242, respectively. The function being minimized is $\sum w(|F_o| - |F_c|)^2$ where the weights, w, are set equal to $1/\sigma^2(F_o)$. Subsequent difference Fourier maps and least-squares refinements revealed the positions of all of the nonhydrogen atoms including an extra water molecule that was probably lost from the analyzed sample when it was dried. Refinement of the positional and isotropic thermal parameters for all 44 atoms resulted in discrepancy factors of $R_1 = 0.142$ and $R_2 = 0.189$. Scattering factors for neutral atoms used in these calculations were taken from the compilation of Cromer and Waber[45] and anomalous dispersion was included for the lead atoms.[46]

At this point an attempt was made to refine the atoms with anisotropic thermal parameters. The result showed no significant improvement in the discrepancy factors, and the thermal parameters of several of the light atoms (O, N, C) became nonpositive definite. Furthermore, a difference Fourier map calculated at this point showed several peaks of the order of 10 e/Å^3 in close proximity to the lead atoms. The lack of improvement of the discrepancy factors, their relatively high values, and the large residual electron density in the difference Fourier map all indicated that although the model structure was probably correct for the most part, there was still something basically wrong since it could not adequately account for the observed intensities.

A careful check of the calculated and observed structure factor lists at this stage revealed an interesting pattern. Many reflections had intensities that were calculated to be small but were observed to be rather large. A representative sample of these reflections can be found in the left-hand column of Table II. It was further noticed that the large observed structure factors for reflections *hkl* having small calculated structure factors were roughly proportional to the observed structure factors for the corresponding $\bar{h}kl$ reflections. This relationship can be seen in Table II. An explanation of these facts was found by invoking a partial twinning on the (100) plane. Every *hkl* reflection collected is in reality a composite of *hkl* and some fraction of its twinned partner $\bar{h}kl$. The effect is most dramatically manifest when the *hkl* reflection is very small and $\bar{h}kl$ is large (compare the F_c columns in Table II). In these cases the intensity observed for *hkl* is mainly derived from its $\bar{h}kl$ twin. It is assumed that this twinning was considerably less than 50% since the model was refined to produce a discrepancy factor R_1 as low as 0.14.

From the original Weissenberg and precession photographs, the compound appeared to be a single crystal. Open-counter 2θ and ω scans on several reflections also did not show any evidence of the twinning. These facts strongly implied that the contributions from both parts of the twin were collected for each reflection. The re-

Table II. Selected Reflections Showing Poor Agreement between F_o and F_c before Introduction of Twinning into the Model[a]

h	k	l	F_o	F_c	h	k	l	F_o	F_c
$\bar{8}$	1	10	41	9	8	1	10	74	82
$\bar{8}$	2	13	60	3	8	2	13	148	152
$\bar{7}$	1	12	76	1	7	1	12	179	198
$\bar{6}$	0	24	54	9	6	0	24	95	80
$\bar{5}$	6	9	93	8	5	6	9	208	223
$\bar{5}$	6	7	99	20	5	6	7	230	251
$\bar{5}$	0	7	153	71	5	0	7	390	415
$\bar{2}$	2	5	140	83	2	2	5	268	266
1	5	22	56	11	$\bar{1}$	5	22	97	92
2	5	13	75	25	$\bar{2}$	5	13	148	141
3	0	1	61	23	$\bar{3}$	0	1	114	101
3	3	7	85	25	$\bar{3}$	3	7	176	179
4	2	12	50	9	$\bar{4}$	2	12	105	130
4	6	8	96	42	$\bar{4}$	6	8	192	215
6	1	7	119	33	$\bar{6}$	1	7	242	270
6	5	9	94	5	$\bar{6}$	5	9	184	204

[a] Values reported are structure factor amplitudes.

finement was therefore modified to account for a partial twinning on the (100) plane in the following manner.

A twinning parameter g was defined as the fraction of the intensity arising from the secondary lattice. Therefore

$$F_{\text{obsd}}(hkl) = [F_o^2(hkl)(1-g) + F_o^2(\bar{h}kl)g]^{1/2}$$

where $F_{\text{obsd}}(hkl)$ is the structure factor as previously obtained from the measured intensities, $F_o(hkl)$ is the structure factor that would be obtained if one were to observe only the major lattice, and $F_o(\bar{h}kl)$ is the structure factor that one would obtain for the reflection $(\bar{h}kl)$ from the major lattice only. It is assumed that this value is equivalent to that for hkl arising from the secondary lattice. Similarly

$$F_{\text{calcd}}(hkl) = [F_c^2(hkl)(1-g) + F_c^2(\bar{h}kl)g]^{1/2}$$

where the terms are analogous to those given above except that they refer to the calculated structure factors. The function minimized in the refinement is

$$M = \sum_{hkl} w_{hkl}[F_{\text{obsd}}(hkl) - F_{\text{calcd}}(hkl)]^2$$

Thus, the observed data were not changed but the calculated model included contributions from a composite lattice.

The least-squares refinement program was then modified to permit variation of the parameter g (see ref 47 for details). Refinement of the same model, including 44 atoms assigned isotropic thermal parameters but allowing for twinning, reduced R_1 to 0.068 and R_2 to 0.072. The twinning parameter, g, refined to 0.164. Allowing the lead atoms to have anisotropic thermal motion lowered R_1 and R_2 to 0.047 and 0.051, respectively. Inclusion of anisotropic thermal parameters for the atoms of the nitrate ions and the water oxygen atoms further lowered the discrepancy factors to 0.044 and 0.047. The carbon and nitrogen atoms of the TPymT ligand were then refined with anisotropic thermal parameters. Although all the parameters refined to convergence, there was only very slight improvement in the discrepancy factors. Application of the Hamilton significance test[48] showed that the hypothesis which states that the TPymT atoms vibrate isotropically could not be rejected with any reasonable confidence. In all subsequent refinements the atoms of TPymT were refined with isotropic thermal parameters.

The composite nature of $F_{\text{obsd}}(hkl)$ and $F_{\text{calcd}}(hkl)$ obscures their true phases making them unsuitable for use in a difference Fourier synthesis. The desired structure factors for comparison are $F_o(hkl)$ and $F_c(hkl)$. The latter was readily available for writing a Fourier input file from the refinement sections of our least-squares program. The least-squares program was further modified to calculate and output the former.

The equations

$$F_{\text{obsd}}^2(hkl) = (1-g)F_o^2(hkl) + gF_o^2(\bar{h}kl)$$

$$F_{\text{obsd}}^2(\bar{h}kl) = (1-g)F_o^2(\bar{h}kl) + gF_o^2(hkl)$$

can be solved simultaneously to yield

$$|F_o(hkl)| = \left[\frac{(1-g)F_{\text{obsd}}^2(hkl) - gF_{\text{obsd}}^2(\bar{h}kl)}{1-2g}\right]^{1/2}$$

where $F_{\text{obsd}}^2(hkl)$ and $F_{\text{obsd}}^2(\bar{h}kl)$ are derived from the measured intensities of the composite reflections indexed as (hkl) and $(\bar{h}kl)$, respectively, and g is the twinning parameter which has already been determined in the least-squares refinement. The errors on the values computed for these observed structure factors are set to be

$$\sigma[F_o(hkl)] = \frac{[\sigma^2[F_{\text{obsd}}^2(hkl)](1-g)^2 + \sigma^2[F_{\text{obsd}}^2(\bar{h}kl)]\,g^2]^{1/2}}{2|F_o(hkl)|}$$

and reflections having values of $|F_o(hkl)|$ less than $3\sigma(F_o(hkl))$ were rejected from the Fourier file. Two hundred eight of the 3184 reflections used in the least-squares refinement were rejected on this basis.

Full-matrix refinement of the scale factors and positional and thermal parameters converged to values for R_1, R_2, and g of 0.044, 0.046, and 0.160 (1), respectively. On the final cycle no parameter varied more than 0.06 of its estimated standard deviation. The final difference Fourier map was noisy. The largest peak was 3.5 e/Å^3 approximately 1 Å from a lead atom. This electron density is approximately 75% of the size of the peak corresponding to the carbon atom with the highest thermal parameter. The standard deviation of the electron density, $\sigma(\rho) = (1/V)\sum \Delta F^2$, was estimated to be 0.38 e/Å^3.[49] No chemical significance is attributed to the remaining peak in the difference Fourier map notwithstanding the fact that it is more than 9 times the standard deviation. No attempt was made to locate hydrogen atoms since their peaks would be indistinguishable from background noise.

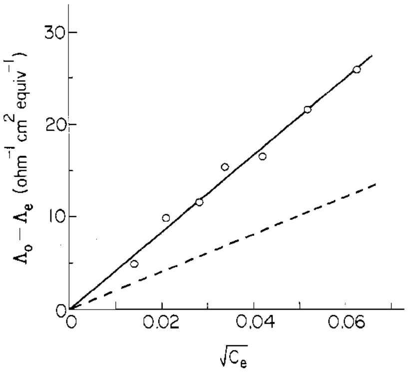


Figure 2. Equivalent conductivity ($\Lambda_0 - \Lambda_e$) of (TPymT)Pb$_2$(NO$_3$)$_4$·2H$_2$O in aqueous solutions (slope 435, solid line). Dashed line represents slope of 200 expected for a 2:1 electrolyte.

Results

Figure 2 shows a plot of equivalent conductance of the dilead complex in water against the square root of equivalent concentration. The data can be fit to the Onsager limiting law,[50] $\Lambda_0 - \Lambda_e = BC_e^{1/2}$. A least-squares fit of the data to the best straight line yielded a slope of 434.9. This value indicates that (TPymT)Pb$_2$(NO$_3$)$_4$·2H$_2$O acts as a 4:1 electrolyte in dilute aqueous solutions. The theoretical value of this slope for a 4:1 electrolyte is 411[51] while a 2:1 electrolyte typically has values about 200.[3]

Figure 3 displays the structure of (TPymT)Pb$_2$(NO$_3$)·2H$_2$O along with the atom- and ring-numbering scheme to which all subsequent discussion will be referred. The final positional and thermal parameters of 44 nonhydrogen atoms of an asymmetric unit are listed in Table III. Table IV contains interatomic bond distances and angles for atoms bonded to

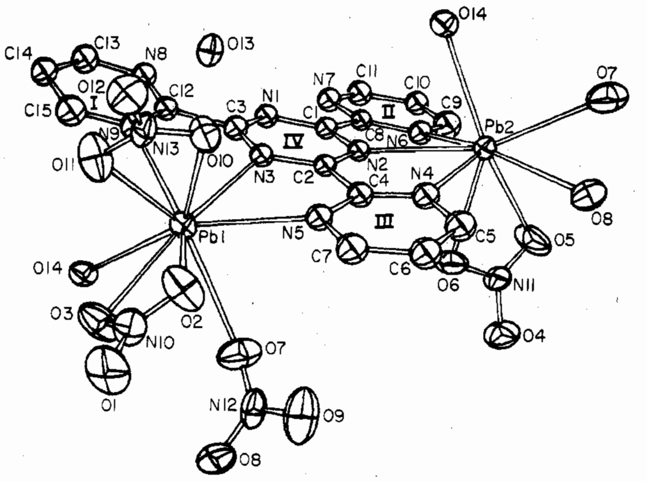


Figure 3. ORTEP drawing of the (TPymT)$Pb_2(NO_3)_4{\cdot}2H_2O$ molecule showing the atom- and ring-labeling schemes and 40% probability thermal ellipsoids.

lead (the coordination spheres). Table V summarizes intra-TPymT bond angles and distances while Table VI contains the corresponding values for the nitrate anions. For comparison, Tables IV–VI also contain the bond distances and angles obtained with the best refinement prior to the introduction of a twinning model into the structural analysis. A tabulation of the values of $F_{obsd}(hkl)$ and $F_{calcd}(hkl)$ can be found in Table S1.[52] Table S2 contains a listing of close nonbonding intermolecular contacts while Table S3 lists the root-mean-square components of thermal displacement along the principal axes for all atoms refined with anisotropic thermal parameters. Table S4 gives the results of least-squares plane calculations on the ring and nitrate portions of the molecule. Table S5 lists the hydrogen-bonding interactions. Figure 4 is a packing diagram showing the contents of one unit cell.

Discussion

The x-ray diffraction results for the lead nitrate complex demonstrate that more than one metal can bind to the 2,4,6-tris(2-pyrimidyl)-1,3,5-triazine ligand. From stoichiometry it appears that three lead atoms (chloride salt), several thallium atoms, and one uranyl group bind to TPymT, but crystallographic work would be required to sustain such conclusions. The choice of the metal and the anion both influence the nature of the product. The ready availability of the ligand by the synthetic method used here will facilitate further study of its metal-binding properties. The structure of (TPymT)$Pb_2(NO_3)_4{\cdot}2H_2O$, discussed below, is stable in aqueous solution where the complex behaves as a 4:1 electrolyte. If the lead atoms dissociated from the ligand, 2:1 electrolytic behavior would be expected.

Description of the Structure

2,4,6-Tris(2-pyrimidyl)-1,3,5-triazinedilead(II) nitrate dihydrate crystallizes in polymeric chains along the crystallographic *b* direction. The distance between lead atoms Pb1 and Pb2 coordinated to a single TPymT molecule is 6.984 (1) Å. The Pb2 atom of one unit is bridged by oxygen atom O14 of a water molecule and by oxygen atom O7 of a nitrate ion to the Pb1 atom of a unit cell translated one unit along the crystallographic *b* axis. The distance between these two lead atoms is 4.148 (1) Å. Figure 5 shows a stereoview of two TPymT$Pb_2(NO_3)_4{\cdot}2H_2O$ units linked together in this manner.

Lead atom Pb1 is surrounded by nine ligating atoms, three nitrogen atoms from the TPymT ligand, five oxygen atoms from nitrate anions, and one oxygen atom from a water molecule. The Pb1 atom–oxygen distances range from 2.56 (1) to 2.87 (1) Å with a mean value of 2.71 Å. These values can be compared to the lead–oxygen distance of 2.805 Å in lead nitrate,[53] the lead–oxygen distance of 2.71 Å in basic lead

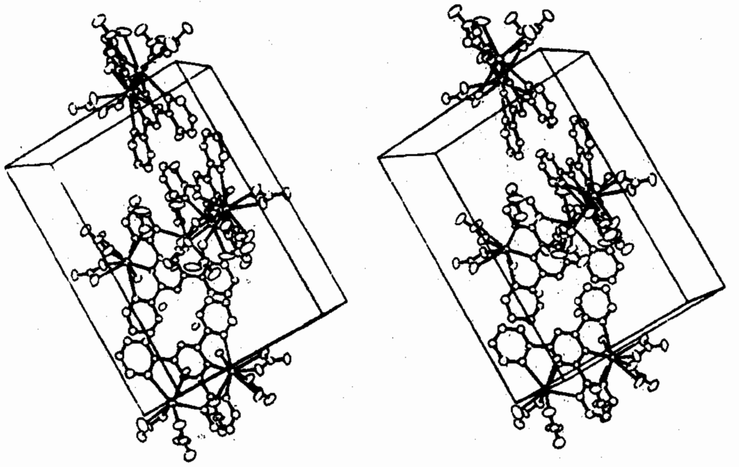


Figure 4. Stereoscopic view of the packing of (TPymT)$Pb_2(NO_3)_4{\cdot}2H_2O$ molecules in a unit cell. The cell outlined extends from $-^1/_4$ to $+^3/_4$, in fractional coordinates, along the crystallographic *a*, *b*, and *c* axes.

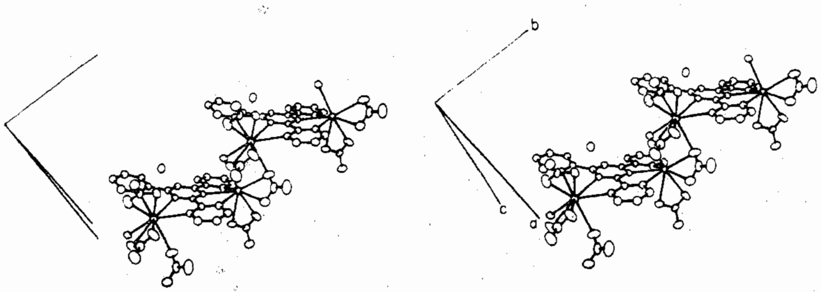


Figure 5. Stereoscopic view of two (TPymT)$Pb_2(NO_3)_4{\cdot}2H_2O$ units showing the bridging between adjacent molecules.

Table III. Final Positional and Thermal Parameters for all Nonhydrogen Atoms in $TPymTPb_2(NO_3)_4 \cdot 2H_2O^{a,b}$

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Pb1	−0.07951 (5)	−0.09206 (9)	0.26805 (3)	4.38 (5)	7.74 (8)	1.542 (17)	0.41 (6)	0.28 (2)	0.08 (4)
Pb2	0.12834 (5)	0.59279 (9)	0.26048 (3)	3.86 (4)	7.98 (8)	1.739 (18)	0.72 (6)	−0.72 (2)	−0.60 (4)
N10	−0.1072 (13)	−0.3202 (20)	0.3821 (8)	7.4 (14)	13 (3)	2.0 (5)	−2.6 (16)	−0.3 (6)	1.4 (9)
N11	0.3218 (11)	0.4617 (17)	0.2919 (8)	2.2 (9)	9 (2)	3.6 (5)	−1.2 (12)	−0.8 (5)	0.8 (8)
N12	0.1264 (13)	−0.2003 (19)	0.3911 (7)	7.1 (13)	13 (3)	1.6 (4)	−4.0 (16)	0.1 (6)	−0.6 (8)
N13	−0.2829 (12)	−0.0629 (16)	0.3010 (7)	4.0 (10)	10 (2)	2.4 (4)	−2.6 (13)	−0.2 (5)	−0.1 (8)
O1	−0.1214 (13)	−0.4084 (17)	0.4291 (6)	13.0 (16)	17 (2)	2.7 (4)	−3.8 (18)	1.1 (6)	3.3 (9)
O2	−0.1201 (12)	−0.1877 (15)	0.3915 (6)	11.0 (14)	12 (2)	2.5 (4)	0.4 (15)	2.6 (6)	0.6 (7)
O3	−0.0828 (13)	−0.3632 (14)	0.3255 (7)	11.8 (16)	11.2 (20)	2.3 (4)	2.7 (14)	1.1 (6)	0.8 (7)
O4	0.3956 (10)	0.3990 (17)	0.3128 (7)	3.5 (8)	17 (2)	4.4 (5)	0.7 (14)	−0.6 (5)	0.7 (9)
O5	0.3171 (11)	0.5887 (16)	0.2768 (9)	6.2 (11)	7.3 (17)	7.8 (8)	−0.7 (13)	−0.7 (7)	2.1 (10)
O6	0.2504 (9)	0.3853 (13)	0.2834 (6)	3.6 (8)	11.3 (19)	3.9 (4)	0.9 (11)	−0.5 (4)	1.8 (7)
O7	0.0960 (11)	−0.1532 (18)	0.3355 (7)	6.7 (12)	25 (3)	2.6 (4)	5.7 (15)	−0.5 (5)	−1.2 (9)
O8	0.1619 (15)	−0.3241 (19)	0.3905 (8)	14.6 (19)	17 (3)	3.9 (5)	3.2 (20)	−4.9 (8)	−0.2 (10)
O9	0.1213 (13)	−0.1320 (18)	0.4437 (7)	11.1 (15)	24 (3)	2.9 (4)	−4.7 (18)	1.3 (6)	−4.0 (10)
O10	−0.2284 (10)	0.0384 (14)	0.3089 (7)	3.3 (8)	10.1 (18)	4.7 (5)	−0.4 (11)	0.9 (5)	−1.4 (8)
O11	−0.2581 (11)	−0.1705 (15)	0.2669 (7)	8.4 (12)	15 (2)	3.2 (5)	−2.2 (13)	2.6 (6)	−2.4 (8)
O12	−0.3635 (10)	−0.0589 (16)	0.3245 (7)	3.6 (8)	17 (2)	3.8 (5)	−0.7 (12)	1.6 (5)	0.3 (8)
O13	−0.0033 (9)	0.2651 (14)	−0.0562 (4)	5.7 (10)	13.1 (18)	1.4 (3)	−1.8 (11)	0.3 (4)	−0.2 (6)
O14	−0.0256 (9)	−0.3245 (12)	0.1871 (5)	4.8 (8)	9.3 (16)	1.4 (3)	0.8 (10)	0.0 (4)	0.4 (5)

Atom	x	y	z	B, Å^2	Atom	x	y	z	B, Å^2
N1	0.0150 (10)	0.2494 (15)	0.0960 (5)	2.5 (2)	C4	0.0123 (12)	0.2629 (18)	0.3081 (7)	2.7 (3)
N2	0.0623 (10)	0.3590 (13)	0.1990 (6)	2.1 (2)	C5	0.0503 (14)	0.3778 (19)	0.4067 (9)	3.7 (4)
N3	−0.0365 (10)	0.1555 (14)	0.2018 (6)	2.3 (2)	C6	0.0109 (14)	0.266 (2)	0.4431 (8)	3.9 (4)
N4	0.0504 (11)	0.3768 (15)	0.3370 (6)	3.0 (3)	C7	−0.0299 (15)	0.149 (2)	0.4085 (9)	3.8 (4)
N5	−0.0293 (11)	0.1483 (15)	0.3382 (6)	2.8 (3)	C8	0.1288 (11)	0.4485 (16)	0.0939 (7)	2.1 (3)
N6	0.1757 (10)	0.5445 (15)	0.1318 (6)	2.8 (3)	C9	0.2321 (15)	0.633 (2)	0.0970 (9)	4.0 (4)
N7	0.1291 (10)	0.4338 (14)	0.0259 (6)	2.9 (3)	C10	0.2374 (13)	0.6300 (18)	0.0254 (8)	3.0 (3)
N8	−0.1131 (10)	0.0684 (14)	0.0312 (6)	2.8 (2)	C11	0.1867 (14)	0.527 (2)	−0.0070 (8)	3.4 (3)
N9	−0.1456 (11)	−0.0391 (15)	0.1366 (6)	3.0 (3)	C12	−0.1022 (12)	0.0554 (17)	0.0974 (7)	2.5 (3)
C1	0.0626 (12)	0.3465 (17)	0.1315 (7)	2.2 (3)	C13	−0.1715 (14)	−0.023 (2)	0.0014 (8)	3.4 (3)
C2	0.0142 (10)	0.2585 (15)	0.2310 (6)	2.1 (2)	C14	−0.2248 (13)	−0.1257 (18)	0.0384 (8)	3.2 (3)
C3	−0.0350 (13)	0.1599 (18)	0.1326 (7)	2.6 (3)	C15	−0.2034 (15)	−0.134 (2)	0.1085 (9)	4.0 (4)

[a] Atom-labeling scheme is as in Figure 3. [b] Numbers in parentheses are errors in the last significant digit(s). The anisotropic temperature factors are $\times 10^3$ and are of the form $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

carbonate,[54] the lead–oxygen distances of 2.59–2.94 Å in bis(thiourea)lead(II) formate,[55] the lead–oxygen distances of 2.7–2.9 Å in lead(II) macroheterocyclic compounds,[56,57] and the sum of the ionic radius of Pb^{2+} and the van der Waals radius of oxygen of 2.67 Å.[58,59] These distances are considered by many workers to be too long for covalent bonding and are referred to as ionic or ion–dipole interaction bonds.[55–57] Examples of tighter covalent bonds between lead(II) and oxygen can be found in tetragonal PbO where the lead–oxygen distance is 2.30 Å,[60] in orthorhombic PbO where the lead–oxygen distance is 2.20 Å,[61,62] and in $Pb_6O(OH)_6(ClO_4)_4 \cdot H_2O$ where the central oxygen atom has an average distance of 2.29 Å from its lead atom neighbors.[63]

The three Pb1 atom–nitrogen bond lengths are 2.70 (1), 2.71 (1), and 2.79 (1) Å for the N3, N5, and N9 nitrogen atoms, respectively, giving an average lead–nitrogen distance of 2.73 Å. These distances are similar to the lead–nitrogen bond lengths of 2.75–2.88 Å in lead(II) macroheterocyclic compounds[56,57] and are considerably longer than the lead–nitrogen bond lengths of 2.21 Å in lead phthalocyanine[64] and 2.24 and 2.29 Å in $Pb(N_2S_2)NH_3$.[65] Again for comparison, the sum of the ionic radius of Pb^{2+} and the van der Waals radius of nitrogen is 2.77 Å.[58,59] The length of these lead–nitrogen bonds, referred to as noncovalent ion–dipole interaction bonds in the macroheterocyclic complexes,[56,57] probably arises from a coordination number effect. Tin(IV), which has ionic and covalent radii that are smaller than those of lead(II),[59] forms a six-coordinate 2,2′,2″-terpyridine (terpy) complex, $[(CH_3)_2SnCl(terpy)]^+$, with an average tin–nitrogen bond length of 2.36 Å[66] and a seven-coordinate terpyridine complex, $[(CH_3)_2Sn(SCN)_2(terpy)]$, where the average tin(IV)–nitrogen bond length is 2.52 Å.[67] Nine-coordinate $[Eu(terpy)_3]^{3+}$ has europium–nitrogen bond lengths that average 2.60 Å[68] and nine-coordinate $[PrCl(H_2O)_5(terpy)]^{2+}$ has praseodymium–nitrogen bond lengths that average 2.63 Å.[69] This effect is also manifest in the present compound where the nine-coordinate Pb1 atom has lead–nitrogen bond lengths that average 2.73 Å while the eight-coordinate Pb2 atom has lead–nitrogen bond lengths that average 2.67 Å (vide infra).

The geometry around the Pb1 atom is quite irregular.[70] If one considers the nitrate anions as occupying one stereochemical position[71,72] and assigns a stereochemical position to the lone pair of electrons on lead(II),[73] the geometry around the Pb1 atom can be described as a distorted cube. One face of the cube is comprised of nitrogen atoms N5, N3, and N9 and the bidentate nitrate anion consisting of the atoms N13, O10, O11, and O12. The opposite face of the cube consists of oxygen atoms O7 and O14, the nitrate anion comprised of atoms N10, O2, O3, and O1, and a lone pair of electrons. Table VII contains a listing of the ligand–metal–ligand angles internal to this cube. The angle subtended at a central metal atom by ligands along an edge of a perfect cube is 70.53°. The angle subtended at the metal atom by ligands diagonally across a face of the cube is 109.47°. The angles subtended by ligands on edges around the Pb1 atom range from 58.8 to 94.0° with an average of 74.6°. The angles subtended by ligands diagonally across the cube faces range from 82.6 to 117.6° with an average of 112.1°. The major sources of distortion in this cube are the constraints placed on the N3, N5, and N9 nitrogen atoms by the rigid tridentate ligand system of which they are a part and the constraints on the O7 and O14 oxygen atoms in being part of a four-membered ring containing the two lead atoms (see Figure 5).

The Pb2 atom is eight-coordinate being bound to three nitrogen atoms of the TPymT ligand, four nitrate oxygen

Table IV. Interatomic Distances (Å) and Angles (deg) around Lead[a] Atoms

Atoms	Twinning model	Previous model	Atoms	Twinning model	Previous model
Distances					
Pb1-N3	2.702 (13)	2.69 (8)	Pb1-O10	2.564 (13)	2.62 (7)
Pb1-N5	2.707 (13)	2.75 (8)	Pb1-O11	2.637 (15)	2.50 (8)
Pb1-N9	2.785 (13)	2.76 (6)	Pb1-O14	2.781 (11)	2.70 (6)
Pb1-O2	2.644 (11)	2.65 (8)	Pb1-O7	2.873 (15)	2.91 (7)
Pb1-O3	2.748 (13)	2.68 (9)			
Pb2-N2	2.645 (12)	2.61 (7)	Pb2-O5	2.698 (16)	2.83 (8)
Pb2-N6	2.654 (13)	2.66 (6)	Pb2-O8	2.705 (14)	2.72 (7)
Pb2-N4	2.733 (14)	2.76 (6)	Pb2-O7	2.809 (15)	2.88 (7)
Pb2-O6	2.622 (12)	2.65 (8)	Pb2-O14	2.722 (12)	2.75 (6)
Angles					
N3-Pb1-N5	59.4 (4)	57.0 (2.2)	N9-Pb1-O11	73.7 (4)	72.7 (2.1)
N3-Pb1-N9	58.8 (4)	61.1 (2.0)	N9-Pb1-O14	72.5 (4)	71.6 (1.8)
N3-Pb1-O2	140.7 (4)	139.7 (2.4)	N9-Pb1-O7	138.6 (4)	140.5 (1.9)
N3-Pb1-O3	166.8 (5)	167.0 (2.5)	O2-Pb1-O3	46.8 (4)	46.9 (2.6)
N3-Pb1-O10	86.6 (4)	84.4 (2.2)	O2-Pb1-O10	71.8 (5)	73.6 (2.3)
N3-Pb1-O11	116.6 (4)	116.6 (2.4)	O2-Pb1-O11	72.7 (5)	73.4 (2.4)
N3-Pb1-O14	108.5 (4)	108.3 (2.1)	O2-Pb1-O14	109.0 (4)	109.6 (2.3)
N3-Pb1-O7	101.1 (5)	100.0 (2.1)	O2-Pb1-O7	72.7 (5)	71.1 (2.3)
N5-Pb1-N9	114.5 (4)	114.3 (2.0)	O3-Pb1-O10	106.6 (5)	108.4 (2.4)
N5-Pb1-O2	82.3 (4)	83.5 (2.4)	O3-Pb1-O11	74.6 (5)	74.8 (2.6)
N5-Pb1-O3	122.9 (4)	124.7 (2.4)	O3-Pb1-O14	62.3 (3)	62.9 (2.3)
N5-Pb1-O10	70.8 (4)	69.4 (2.2)	O3-Pb1-O7	69.4 (5)	70.4 (2.3)
N5-Pb1-O11	118.8 (4)	118.5 (2.4)	O10-Pb1-O11	48.6 (4)	49.7 (2.4)
N5-Pb1-O14	148.4 (4)	147.1 (2.1)	O10-Pb1-O14	140.4 (4)	142.5 (2.0)
N5-Pb1-O7	72.6 (4)	71.4 (2.1)	O10-Pb1-O7	131.5 (4)	129.3 (2.0)
N9-Pb1-O2	146.5 (5)	146.1 (2.2)	O11-Pb1-O14	92.8 (4)	94.3 (2.3)
N9-Pb1-O3	122.3 (4)	120.7 (2.2)	O11-Pb1-O7	141.4 (5)	141.6 (2.2)
N9-Pb1-O10	86.1 (4)	85.7 (1.9)	O14-Pb1-O7	82.6 (4)	84.3 (1.9)
N2-Pb2-N6	61.3 (4)	59.8 (2.0)	N4-Pb2-O5	109.1 (4)	108.8 (2.3)
N2-Pb2-N4	60.7 (4)	63.2 (1.9)	N4-Pb2-O8	76.1 (5)	73.6 (2.1)
N2-Pb2-O6	73.4 (4)	73.4 (2.2)	N4-Pb2-O7	104.8 (5)	105.6 (2.0)
N2-Pb2-O5	113.2 (4)	111.0 (2.4)	N4-Pb2-O14	99.8 (4)	103.1 (1.9)
N2-Pb2-O8	136.3 (5)	136.6 (2.2)	O6-Pb2-O5	46.7 (4)	47.9 (2.6)
N2-Pb2-O7	149.7 (4)	152.2 (2.1)	O6-Pb2-O8	86.1 (5)	86.4 (2.3)
N2-Pb2-O14	72.9 (4)	74.8 (2.0)	O6-Pb2-O7	129.0 (4)	127.5 (2.2)
N6-Pb2-N4	120.3 (4)	121.0 (1.9)	O6-Pb2-O14	145.6 (4)	147.9 (2.2)
N6-Pb2-O6	82.6 (4)	84.3 (2.1)	O5-Pb2-O8	73.7 (6)	78.9 (2.3)
N6-Pb2-O5	81.7 (5)	79.1 (2.1)	O5-Pb2-O7	96.5 (5)	96.7 (2.4)
N6-Pb2-O8	154.3 (6)	156.7 (2.1)	O5-Pb2-O14	149.5 (4)	146.5 (2.2)
N6-Pb2-O7	133.0 (4)	132.2 (2.0)	O8-Pb2-O7	45.3 (4)	44.4 (2.1)
N6-Pb2-O14	75.5 (4)	76.0 (1.9)	O8-Pb2-O14	123.9 (5)	120.6 (2.1)
N4-Pb2-O6	68.9 (4)	65.9 (2.2)	O7-Pb2-O14	84.9 (4)	84.0 (2.0)

[a] See footnotes *a* and *b* in Table III.

atoms, and an oxygen atom from a water molecule. The Pb2 atom–oxygen bond lengths range from 2.62 (1) to 2.81 (2) Å with the average Pb2 atom–oxygen distance being 2.71 Å. The three Pb2 atom–nitrogen bond lengths are 2.64 (1), 2.73 (1), and 2.65 (1) Å for nitrogen atoms N2, N4, and N6, respectively. The average Pb2 atom–nitrogen distance is 2.67 Å. The geometry around this lead atom can be described as a pentagonal bipyramid if one again considers nitrate anions as occupying only one stereochemical position. Nitrogen atoms N2, N4, and N6, the nitrate anion consisting of atoms N12, O7, O8, and O9, and a stereochemically active lone pair of electrons on the lead atom[73] form the pentagonal plane around the Pb2 atom. An oxygen atom from water, O14, and the nitrate anion consisting of atoms N11, O4, O5, and O6 bind in the axial positions. The angles N2–Pb2–N4 and N2–Pb2–N6, 60.9 (4) and 61.3 (4)°, respectively, are smaller than the 72° expected in a pentagonal plane. This distortion is presumably caused by their being part of a rigid tridentate ligand system. The line joining the N12 nitrogen atom of the equatorial nitrate anion and the lead atom makes an angle of 89.5 (4)° with the Pb–N4 bond axis. A space of 150.0 (4)° remains to be occupied by the equatorial lone pair of electrons. This value compares well with a space of 152.3° for the lone pair of electrons in lead(II) *O*,*O*′-diisopropyl phosphorodithioate in which the lead atom also has a pentagonal-bipyramidal coordination geometry with a pair of electrons in one of the pentagonal positions.[73] The axial oxygen atom, O14, is distorted from the perpendicular. It makes angles of 72.9 (4), 99.8 (4), and 75.5 (4)°, respectively, with nitrogen atoms N2, N4, and N6. This distortion is probably caused by oxygen atom O14 being part of the four-membered ring that bridges the two lead atoms.

The bond lengths and angles in the TPymT ligand are all typical values expected for nitrogen heterocycles. The external ring angles N3–C2–C4, N3–C3–C12, N2–C2–C4, and N2–C1–C8 all lie between 115 and 118°. As expected, these values indicate little angular strain in the ligand as it forms long metal–nitrogen bonds. Complexes of terpyridine with metals that necessitate short metal–nitrogen bonds have considerable strain in the comparable external ring angles while those with relatively long metal–nitrogen bonds do not exhibit as much strain. Cyano(2,2′,2″-terpyridine)copper(II) nitrate monohydrate, which has an average copper(II)–nitrogen bond length of 2.02 Å, has external ring angles of 111 and 110°.[74] 2-Hydroxyethanethiolato(2,2′,2″-terpyridine)platinum(II) nitrate has external ring angles of 112.6 and 113.0° while the average platinum–nitrogen distance is 2.00 Å.[3] (Dimethyl diisothiocyanato)(2,2′,2″-terpyridine)tin(IV), however, which has an average metal–nitrogen distance of 2.52 Å, has relatively unstrained angles of 116° each.[67]

Table V. Intraligand Distances (Å) and Angles (deg)[a]

Atoms	Twinning model	Previous model
	Distances	
N1-C1	1.321 (19)	1.44 (11)
N1-C3	1.31 (2)	1.31 (9)
N2-C1	1.330 (16)	1.21 (10)
N2-C2	1.313 (18)	1.41 (9)
N3-C2	1.323 (18)	1.31 (10)
N3-C3	1.359 (18)	1.42 (9)
N4-C4	1.31 (2)	1.23 (9)
N4-C5	1.37 (2)	1.34 (11)
N5-C4	1.35 (2)	1.29 (10)
N5-C7	1.38 (2)	1.42 (10)
N6-C8	1.334 (19)	1.32 (10)
N6-C9	1.33 (2)	1.41 (12)
N7-C8	1.341 (17)	1.25 (10)
N7-C11	1.35 (2)	1.39 (11)
N8-C12	1.313 (18)	1.28 (11)
N8-C13	1.32 (2)	1.28 (10)
N9-C12	1.32 (2)	1.43 (11)
N9-C15	1.32 (2)	1.32 (13)
C1-C8	1.52 (2)	1.57 (12)
C2-C4	1.512 (17)	1.59 (9)
C3-C12	1.52 (2)	1.47 (12)
C5-C6	1.38 (2)	1.39 (14)
C6-C7	1.40 (2)	1.31 (12)
C9-C10	1.41 (2)	1.49 (13)
C10-C11	1.35 (2)	1.37 (12)
C13-C14	1.41 (2)	1.39 (11)
C14-C15	1.41 (2)	1.43 (13)
	Angles	
C3-N1-C1	114.7 (1.2)	117 (7)
C1-N2-C2	114.8 (1.3)	117 (7)
C2-N3-C3	113.7 (1.3)	115 (7)
C4-N4-C5	115.9 (1.4)	115 (7)
C7-N5-C4	115.9 (1.4)	109 (7)
C8-N6-C9	115.1 (1.4)	116 (7)
C8-N7-C11	114.6 (1.4)	115 (8)
C12-N8-C13	116.8 (1.4)	120 (8)
C12-N9-C15	119.1 (1.4)	116 (8)
N1-C1-N2	125.5 (1.4)	124 (8)
N1-C1-C8	118.7 (1.2)	114 (7)
N2-C1-C8	115.7 (1.3)	121 (8)
N2-C2-N3	125.7 (1.2)	125 (6)
N2-C2-C4	118.0 (1.3)	116 (6)
N3-C2-C4	116.2 (1.3)	118 (6)
N3-C3-N1	125.4 (1.5)	120 (6)
N3-C3-C12	115.0 (1.4)	118 (7)
N1-C3-C12	119.5 (1.3)	122 (7)
N5-C4-N4	128.3 (1.3)	134 (7)
C2-C4-N4	116.5 (1.4)	119 (6)
C2-C4-N5	115.2 (1.3)	107 (6)
N4-C5-C6	121.0 (1.6)	121 (9)
C5-C6-C7	119.7 (1.5)	115 (9)
C6-C7-N5	119.2 (1.6)	124 (8)
N6-C8-N7	128.1 (1.4)	135 (8)
C1-C8-N6	116.8 (1.3)	109 (7)
C1-C8-N7	115.0 (1.3)	116 (7)
N6-C9-C10	122.1 (1.7)	112 (8)
C9-C10-C11	117.0 (1.6)	125 (9)
C10-C11-N7	123.0 (1.5)	118 (8)
N9-C12-N8	125.8 (1.5)	124 (9)
C3-C12-N8	117.6 (1.4)	119 (8)
C3-C12-N9	116.6 (1.3)	117 (7)
N8-C13-C14	122.5 (1.6)	122 (7)
C13-C14-C15	115.0 (1.6)	117 (8)
C14-C15-N9	120.3 (1.6)	119 (10)

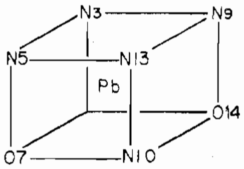
[a] See footnotes *a* and *b* in Table III.

Table VI. Interatomic Distances (Å) and Angles (deg) within the Nitrate Anions[a]

Atoms	Twinning model	Previous model
	Distances	
N10-O1	1.247 (18)	1.35 (12)
N10-O2	1.25 (2)	1.15 (11)
N10-O3	1.230 (19)	1.33 (11)
N11-O4	1.264 (19)	1.25 (9)
N11-O5	1.212 (18)	1.28 (11)
N11-O6	1.245 (18)	1.23 (10)
N12-O7	1.251 (18)	1.22 (10)
N12-O8	1.25 (2)	1.21 (10)
N12-O9	1.211 (18)	1.23 (11)
N13-O10	1.224 (18)	1.26 (10)
N13-O11	1.249 (18)	1.25 (11)
N13-O12	1.24 (2)	1.27 (10)
	Angles	
O1-N10-O2	120.4 (1.7)	123 (10)
O1-N10-O3	120.2 (1.8)	115 (9)
O2-N10-O3	119.4 (1.5)	118 (10)
O4-N11-O5	124.6 (1.7)	117 (8)
O4-N11-O6	117.1 (1.5)	116 (8)
O5-N11-O6	118.2 (1.6)	125 (8)
O7-N12-O8	116.6 (1.6)	122 (9)
O7-N12-O9	122.7 (2.1)	123 (9)
O8-N12-O9	120.8 (1.8)	115 (9)
O10-N13-O11	119.9 (1.6)	118 (9)
O10-N13-O12	121.0 (1.6)	118 (9)
O11-N13-O12	119.1 (1.5)	123 (9)

[a] See footnotes *a* and *b* in Table III.

Table VII. Geometry around Pb1 Idealized to Cubic Symmetry (See Text)[a]



Angles (deg) subtended at Pb atom by ligands across cube edges		Angles (deg) subtended at Pb atom by ligands across cube-face diagonal	
N3-Pb1-N5	59.4	N3-Pb1-N13	104.4
N3-Pb1-N9	58.8	N3-Pb1-O7	101.1
N5-Pb1-N13	94.0	N3-Pb1-O14	108.5
N9-Pb1-N13	82.0	N5-Pb1-N9	114.5
N5-Pb1-O7	72.6	N5-Pb1-N10	103.0
N13-Pb1-N10	77.2	N9-Pb1-N10	138.1
N9-Pb1-O14	72.5	O7-Pb1-N13	139.4
O7-Pb1-N10	69.2	O7-Pb1-O14	82.6
O14-Pb1-N10	85.6	O14-Pb1-N13	117.6
Average	74.6	Average	112.1
For perfect cube:	70.53°	For perfect cube:	109.47°

[a] See footnotes *a* and *b* in Table III.

The individual pyrimidine and triazine rings of the TPymT ligand are planar. The greatest deviation of an atom from the mean plane of each individual ring is 0.04 (2) Å. The entire molecule, however, is not quite planar. Calculation of a mean plane through all of the atoms of the ligand shows that individual atoms deviate from the best plane by as much as 0.30 (1) Å. The Pb1 atom is 1.1997 (7) Å below that plane while the Pb2 atom is 0.8257 (7) Å above it. The dihedral angles between the three pyrimidine rings and the triazine ring are defined such that the angle is positive for a clockwise rotation around the bond between the individual pyrimidine ring and the triazine ring when viewed from the pyrimidine ring. The dihedral angles made by the mean planes of pyrimidine rings I, II, and III (Figure 3) with the mean plane of the triazine ring are 10.8, 4.2, and -9.2°, respectively. The Pb1 atom is 0.9462 (7) Å below the plane of the triazine ring while the Pb2 atom is 0.5587 (7) Å above that plane. This type of puckering, albeit to a lesser extent, is known to occur in some complexes of terpyridine.[66,67,74] Related to the large puckering of the rings is the length of the lead–nitrogen bonds. The rings that contain the nitrogen atoms that bond to Pb1 (which has an average lead–nitrogen distance of 2.73 Å) are twisted 10.8

and 9.2° while the rings that contain the nitrogen atoms that bond Pb2 (at an average distance of 2.67 Å) are twisted 9.2 and 4.2°. Somewhat shorter metal–nitrogen bonds would therefore presumably lessen this twisting.

The nitrate anions have their expected trigonal geometry. They are planar with no deviations greater than 0.02 (1) Å from their individual mean planes. The nitrogen–oxygen bond lengths average 1.24 Å and the oxygen–nitrogen–oxygen angles average 120°. We do not, however, find that the nitrogen–oxygen bond distance is longer for metal–bound oxygen atoms than for unbound ones (Table VI) as reported elsewhere.[72,75,76]

An interesting feature of this structure is the mode of bridging between the lead atoms. Lead atoms Pb1 and Pb2 are bridged by an oxygen atom from a water molecule[77] and by a single oxygen of a nitrate anion. This mode of bridging is rare for nitrate groups.[72] However, a similar mode of bridging using a single oxygen of a carboxylate anion has been observed in lead(II) chemistry. A single oxygen atom of a formate anion bridges two lead atoms in bis(thiourea)lead(II) formate monohydrate.[55] The formate oxygen atom binds one lead atom at a distance of 2.75 Å and another at a distance of 2.94 Å. The same mode of binding was also found in the crystal structure of mono(thiourea)lead(II) acetate.[78] In that case a single carboxylate oxygen atom binds two lead atoms at distances of 2.63 and 3.01 Å. In the present structure the nitrate oxygen atom binds one lead atom at 2.87 (1) Å and the other at 2.81 (2) Å.

No hydrogen atoms were located in the structure determination. Hydrogen bonding interactions may be assessed from the proximity and disposition of the atoms to which the hydrogens are attached. Oxygen atom O13 is not bound to either lead atom. It is found within the third terpyridine-like site of the molecule and is assumed to be part of a water molecule from stoichiometric considerations. Atom O13 is 2.92 (2) Å from nitrogen atom N7 and 2.95 (2) Å from nitrogen atom N8, the angle N7–O13–N8 is 110.4 (4)° (Figure 3). These facts imply that this water molecule is hydrogen bonded to both N7 and N8. Oxygen atom O14 is 2.66 (1) Å from oxygen atom O13 at position $\bar{x}, \bar{y}, \bar{z}$, 2.69 (2) Å from oxygen atom O12 at position $-{}^1/_2 - x, -{}^1/_2 + y, {}^1/_2 - z$, 2.77 (2) Å from oxygen atom O4 at position ${}^1/_2 - x, {}^1/_2 + y, {}^1/_2 - z$, and 2.86 (2) Å from oxygen atom O3. The hydrogen atoms on oxygen atom O14 could therefore be hydrogen bonded to any of these oxygen atoms. The angles O13($\bar{x}, \bar{y}, \bar{z}$)–O14–O12($-{}^1/_2 - x, -{}^1/_2 + y, {}^1/_2 - z$) and O13($\bar{x}, \bar{y}, \bar{z}$)–O14–O3 are 100.2 (5) and 106.5 (5)°, respectively, making their combinations the most likely candidates for hydrogen bonding from oxygen atom O14.

A comparison of the structure before and after the introduction of twinning into the model shows that the basic geometry is essentially unchanged. As can be seen in Tables IV–VI the values for bond distances and angles are very similar for the two models. The errors of the values in the nontwinning model are considerably greater than the final values. In all cases the final values were within three pretwin estimated standard deviations of the pretwin values.

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Registry No. (TPymT)Pb$_2$(NO$_3$)$_4$·2H$_2$O, 62358-61-6; (TPymT)UO$_2$(NO$_3$)$_2$, 62288-66-8; (TPymT)Pb$_3$Cl$_6$, 62288-67-9; (TPymT)$_2$Tl$_7$(NO$_3$)$_7$, 62358-60-5; 2,4,6-tris(2-pyrimidyl)-1,3,5-triazine, 60681-68-7.

Supplementary Material Available: Tables S1–S5 giving structure factor amplitudes, nonbonding intermolecular contacts, rms amplitudes of thermal vibration, best planes and dihedral angles, and possible H-bonding interactions (25 pages). Ordering information is given on any current masthead page.

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Hydrolysis Reactions of 2,4,6-Tris(2-pyrimidyl)- and 2,4,6-Tris(2-pyridyl)-1,3,5-triazines with Divalent Copper. Structure of a Bis(2-pyrimidylcarbonyl)aminatocopper(II) Complex

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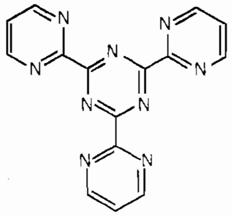
The compounds 2,4,6-tris(2-pyrimidyl)- and 2,4,6-tris(2-pyridyl)-1,3,5-triazine were found to undergo hydrolysis reactions in the presence of divalent copper. The products of these reactions are bis(arylcarbonyl)aminatocopper(II) complexes and the free arylamides. Crystals of bis(2-pyrimidylcarbonyl)aminatotriaquocopper(II) nitrate dihydrate were grown from aqueous solutions of the compound. The blue complex of formula $[Cu(C_{10}H_6N_5O_2)(H_2O)_3](NO_3)\cdot 2H_2O$ crystallizes in the triclinic space group $P\bar{1}$ with two formulas per unit cell. Lattice parameters are $a = 13.626$ (3) Å, $b = 6.512$ (1) Å, $c = 10.497$ (2) Å, $\alpha = 101.48$ (1)°, $\beta = 109.32$ (1)°, and $\gamma = 94.83$ (1)°. By use of 3385 unique observed reflections collected by diffractometer, the structure was solved and refined to a final value of 0.030 for the discrepancy factor R_1. The copper atom is coordinated by a distorted octahedral array of ligand atoms. Three nitrogen atoms from the new ligand and one water molecule form a distorted square plane around the copper while two weakly bound water molecules occupy the axial positions. Angular strain at the carbonyl carbon atoms in the coordinated bis(2-pyrimidylcarbonyl)aminato ligand suggests a mechanistic role by which copper(II) assists the hydrolysis of the normally stable 2,4,6-triaryl-1,3,5-triazines.

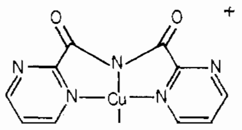
Introduction

During the course of preparing and characterizing heavy-metal complexes of the ligand 2,4,6-tris(2-pyrimidyl)-1,3,5-triazine, TPymT, described in the preceding paper,[1]



TPymT

an interesting reaction was observed with divalent copper. In particular, copper(II) was found to promote the hydrolysis of the TPymT ligand to form a novel bis(2-pyrimidylcarbonyl) aminato chelate complex[2]



A similar reaction takes place with the related 2,4,6-tris(2-pyridyl)-1,3,5-triazine ligand, TPyT, resulting in a bis(2-pyridylcarbonyl)aminatocopper(II) complex. Crystals of both complexes were obtained. The present article describes their properties and the x-ray structure determination of bis(2-pyrimidylcarbonyl)aminatotriaquocopper(II) nitrate dihydrate. As discussed in a preliminary report,[2] several other metal ions promote the hydrolysis of these triazines, but their chemistry has not been further investigated.

Experimental Section

The materials for this study were of reagent grade and were used without further purification. 2,4,6-Tris(2-pyrimidyl)-1,3,5-triazine was synthesized as previously described.[1,2] Infrared spectra were taken on JASCO IRA-1 and Perkin-Elmer 137 and 621 spectrophotometers and were calibrated with polystyrene. Mass spectra were taken on a JEOL JMS-07 EI mass spectrometer.

Hydrolysis of TPymT with Copper to Form $[Cu(C_{10}H_6N_5O_2)(H_2O)_3](NO_3)\cdot 2H_2O$. The synthesis and analytical data for this compound were reported previously.[2] It has the following bands in the infrared spectrum (Nujol mull): 3450 (br, m), 3060 (w), 1726 (s), 1663 (w), 1623 (m), 1578 (s), 1562 (w), 1380 (br, under Nujol peak), 1200 (m), 1114 (w), 1076 (w), 1044 (w), 1030 (w), 1005 (w), 855 (w), 830 (w), 715 (m), 675 (m) cm^{-1}.

Hydrolysis of TPyT with Copper to Form $[Cu(C_{12}H_8N_3O_2)(H_2O)_3](NO_3)\cdot 1.5H_2O$. The synthesis, analytical data, and dehydration weight loss of this compound were described previously.[2] Its infrared spectral bands (Nujol mull) appear at 3400 (br, m), 1710 (s), 1665 (m), 1640 (m), 1600 (s), 1570 (m), 1380 (br, under Nujol peak), 1150 (w), 1090 (w), 1045 (w), 1025 (m), 1000 (w), 968 (w), 815 (m), 792 (w), 753 (m), and 698 (m) cm^{-1}.

Extraction of the blue reaction mixture with benzene yielded, upon drying and removal of the benzene, a white powder. The infrared spectrum and mass spectrum (M^+ 122) identified the major product as 2-picolinamide. IR ($CHCl_3$ solution): 3559 (w), 3413 (w), 3030