Table III. Positional Parameters and Their Estimated Standard Deviations for **3**

atom	*x*	*y*	*z*	*B*, Å^2
Cr	0.95337 (5)	0.08155 (4)	0.91877 (4)	1.88 (1)
Na(1)	1.1198 (1)	−0.0517 (1)	0.8739 (1)	2.07 (3)
Na(2)	0.8630 (1)	−0.0968 (1)	0.9215 (1)	2.11 (3)
O(1)	0.9571 (2)	−0.0063 (2)	0.8192 (2)	1.98 (6)
O(2)	0.8209 (2)	0.0422 (2)	0.9482 (2)	2.19 (6)
O(3)	1.0964 (2)	0.1002 (2)	0.9134 (2)	2.32 (6)
O(4)	0.9663 (2)	0.1458 (2)	1.0404 (2)	2.15 (6)
O(5)	1.2334 (2)	−0.0939 (2)	0.7763 (2)	3.06 (7)
O(6)	0.7412 (2)	−0.1870 (2)	0.8782 (2)	3.25 (8)
C(1)	0.9064 (3)	−0.0160 (3)	0.7330 (3)	1.82 (8)
C(2)	0.8056 (3)	−0.0030 (4)	0.7166 (3)	3.3 (1)
C(3)	0.7562 (4)	−0.0162 (4)	0.6269 (4)	4.3 (1)
C(4)	0.8054 (4)	−0.0416 (3)	0.5501 (3)	3.3 (1)
C(5)	0.9054 (4)	−0.0540 (3)	0.5651 (3)	3.01 (1)
C(6)	0.9553 (3)	−0.0411 (3)	0.6544 (3)	2.5 (1)
C(7)	0.7350 (3)	0.0841 (3)	0.9431 (3)	2.03 (8)
C(8)	0.7304 (3)	0.1705 (3)	0.9465 (3)	2.6 (1)
C(9)	0.6407 (4)	0.2110 (3)	0.9423 (3)	3.3 (1)
C(10)	0.5533 (3)	0.1662 (4)	0.9354 (3)	3.4 (1)
C(11)	0.5567 (3)	0.0814 (4)	0.9303 (3)	3.3 (1)
C(12)	0.6463 (3)	0.0396 (3)	0.9336 (3)	2.6 (1)
C(13)	1.1481 (3)	0.1212 (3)	0.8402 (3)	1.85 (8)
C(14)	1.1040 (3)	0.1386 (3)	0.7489 (3)	2.31 (9)
C(15)	1.1599 (4)	0.1615 (3)	0.6752 (3)	3.2 (1)
C(16)	1.2606 (4)	0.1665 (4)	0.6913 (3)	3.8 (1)
C(17)	1.3060 (3)	0.1455 (4)	0.7808 (3)	3.7 (1)
C(18)	1.2509 (3)	0.1231 (3)	0.8550 (3)	2.9 (1)
C(19)	0.9831 (3)	0.2260 (3)	1.0584 (3)	1.88 (9)
C(20)	1.0164 (3)	0.2515 (3)	1.1527 (3)	2.24 (9)
C(21)	1.0334 (3)	0.3337 (3)	1.1740 (4)	3.2 (1)
C(22)	1.0173 (4)	0.3939 (3)	1.1051 (4)	3.8 (1)
C(23)	0.9850 (4)	0.3701 (3)	1.0119 (4)	3.7 (1)
C(24)	0.9701 (3)	0.2869 (3)	0.9886 (3)	2.7 (1)
C(25)	1.2197 (6)	−0.1169 (7)	0.6755 (6)	4.0 (2)
C(25′)	1.2275 (9)	−0.073 (1)	0.6727 (9)	4.0 (3)
C(26)	1.3235 (6)	−0.1333 (7)	0.6485 (6)	3.9 (2)
C(26′)	1.3339 (8)	−0.071 (1)	0.6454 (9)	3.9 (3)
C(27)	1.3890 (4)	−0.0993 (6)	0.7246 (5)	7.3 (2)
C(28)	1.3362 (4)	−0.1000 (4)	0.8118 (4)	4.5 (1)
C(29)	0.7279 (4)	−0.2621 (4)	0.9316 (4)	3.8 (1)
C(30)	0.6349 (5)	−0.2990 (4)	0.8859 (4)	5.2 (2)
C(31)	0.6471 (8)	−0.2798 (6)	0.7802 (5)	9.4 (3)
C(32)	0.7005 (5)	−0.2005 (5)	0.7820 (4)	5.8 (2)

Table IV. Selected Bond Distances (Å) and Angles (deg)

complex 1		complex 3	
Cr–O(1)	1.948 (2)	Cr–O(1)	1.990 (3)
Cr–O(3)	2.097 (2)	Na(2)–O(1)	2.488 (3)
O(1)–Cr–O(2)	170.44 (9)	Na(2)–O(6)	2.247 (4)
O(2)–Cr–O(3)	94.73 (9)	O(1)–Cr–O(2)	90.3 (1)
O(3)–Cr–O(4)	177.8 (1)	O(1)–Na(2)–O(2)	71.6 (1)
Cr–O(1)–C(1)	147.6 (2)	O(1)–Na(2)–O(6)	129.3 (1)
Cr–O(2)–C(16)	139.7 (2	Cr···Cr′	3.622 (1)
		Cr···Na(2)	3.120 (7)
		Na(1)···Na(2)	3.711 (2)

solid dissolved, forming a purple solution. After evaporation to dryness and recrystallization of the resulting purple solid from toluene/TMEDA (10:1), purple crystals of **2** separated on cooling (0.42 g, 0.46 mmol, 46% yield). Anal. Calcd (found) for $C_{51}H_{76}O_4N_4Na_2Cr$: C, 67.55 (67.31); H, 8.39 (8.51); Cr, 5.71 (5.74); N, 6.18 (6.11); Na, 5.08 (5.39). IR (Nujol mull, KBr, cm^{-1}): 1585 (s), 1405 (s), 1260 (m), 1250 (m), 1210 (m), 1185 (m), 1160 (w), 1150 (w), 1110 (w), 1070 (s), 1020 (w), 1005 (s), 925 (m), 825 (s), 725 (s), 670 (s), 585 (m), 510 (s), 450 (m). $\mu_{eff} = 3.45\ \mu_B$.

[(OPh)$_8$Cr$_2$(Na·THF)$_4$] (3). In a standard experiment, a suspension of PhONa in THF (75 mL) [obtained by reacting 0.80 g of NaH (33.3 mmol) with 3.14 g of phenol (33.4 mmol)], was reacted with $CrCl_2(THF)_2$ (2.20 g, 8.24 mmol). The resulting purple mixture was stirred for 1.5 h, filtered, and cooled at −30 °C. The well-formed purple crystals, which lost solvent under an N_2 stream, were pumped in vacuo, forming a green pyrophoric solid. Green crystals were obtained upon recrystallization from toluene/THF mixtures (4:1) (3.74 g, 3.0 mmol, 74% yield). Anal. Calcd (found) for $C_{64}H_{72}O_{12}Cr_2Na_4$: C, 61.99 (62.42); H, 6.45 (5.99); Cr, 8.38 (7.94); Na, 7.42 (7.30). IR [Nujol mull, KBr, cm^{-1}]: 1590 (s) 1485 (s) 1270 (s) 1160 (m) 1050 (m) 990 (w) 840 (m) 835 (w) 760 (s) 695 (s) 885 (s). $\mu_{eff} = 2.84\ \mu_B$.

X-ray Crystallographic Studies

All X-ray data were collected on Enraf-Nonius CAD-4F fully automatic diffractometers equipped with locally modified low-temperature devices. Scaling factors and Lorentz and polarization corrections were applied to the data. No absorption corrections were necessary. Details on crystal data and refinement are given in Table I.

Crystal Data for $C_{38}H_{62}O_4Cr$ (1). $M_R = 634.90$, monoclinic, space group $P2_1/n$, $a = 10.218$ (1) Å, $b = 23.308$ (4) Å, $c = 16.033$ (1) Å, $\beta = 99.96$ (1)°, $V = 3760.9$ (8) Å^3, $Z = 4$, $D_c = 1.121$ g/cm^{-3}, $F(000) = 1384$, Zr-filtered Mo Kα radiation with λ = 0.71073 Å, and μ(Mo Kα) = 3.3 cm^{-1}. Intensities of 13955 reflections were collected ($2\theta_{max} = 50°$, $\omega/2\theta$ scan) at 295 K. A total of 3981 independent reflections with $I > 2.5\sigma(I)$ were used in the structure determination. The structure was solved by direct methods (SHELXS86) and refined by blocked full-matrix least-squares techniques (SHELX76) to $R = 0.0533$, ($R_w = 0.0478$). All of the hydrogen atoms were introduced at calculated positions with C–H = 0.98 Å and included in the refinement with three isotropic thermal parameters. Positional and thermal parameters are given in Table II.

Crystal Data for $(C_{32}H_{36}O_6Na_2Cr)_2$ (3). $M_R = 1229.23$, monoclinic, space group $P2_1/n$, $a = 13.680$ (5) Å, $b = 16.078$ (3) Å, $c = 14.009$ (4) Å, $\beta = 95.59$ (2)°, $V = 3066.6$ (5) Å^3, $Z = 2$, $D_c = 1.33$ g/cm^3, and $F(000) = 1288$. Data were measured ($2\theta_{max} = 50°$) at low temperature (130 K) by using graphite-filtered Mo Kα radiation (λ = 0.71073 Å) and scan type θ–2θ. A total of 4171 independent reflections with $I > 3\sigma(I)$ were used in the structure determination. The structure was partly solved by direct methods. The positions of the remaining atoms were revealed from succeeding Fourier difference maps. Block-diagonal least-squares techniques were used in the refinement. All the non-hydrogen atom positions were refined anisotropically. All the hydrogen atoms were introduced at calculated positions with C–H = 0.98 Å and included in the refinement with three isotropic thermal parameters. The final *R* values converged to $R = 0.047$ ($R_w = 0.059$). Positional and thermal parameters are given in Table III.

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Registry No. **1**, 119365-62-7; **2**, 119010-41-2; **3**, 119010-44-5; $CrCl_2(THF)_2$, 15604-50-9; $MeS_2Cr(THF)_3$, 15604-48-5; $(PhO)_4CrNa_2(THF)_4$, 119327-38-7; $(PhO)_4CrNa_2(py)_4$, 119327-40-1; $(PhO)_4CrNa_2(^1/_2TMEDA)_4$, 119327-42-3; $[2,6\text{-}(CH_3)_2C_6H_3O]_4CrNa_2(THF)_4$, 119327-43-4; $[2,6\text{-}(CH_3)_2C_6H_3O]_4CrNa_2(py)_4$, 119327-44-5; (β-naphthyl-O)$CrNa_2(THF)_4$, 119327-45-6; (β-naphthyl-O)$CrNa_2(py)_4$, 119327-46-7; (β-naphthyl-O)$CrNa_2(^1/_2TMEDA)_4$, 119327-47-8; $(PhO)_8Cr(Na\cdot py)_4$, 119010-47-8; (β-naphthyl-O)$_8Cr_2(Na\cdot THF)_4$, 119038-53-8; (β-naphthyl-O)$_8Cr_2(Na\cdot py)_4$, 119327-48-9.

Supplementary Material Available: Complete listings of crystal data, positional atomic parameters, thermal parameters, and bond distances and angles for **1** and **3** and torsion angles for **1** and an ORTEP drawing for **3** showing all the non-hydrogen atoms with the labeling scheme (17 pages); listings of observed and calculated structure factors for complexes **1** and **3** (61 pages). Ordering information is given on any current masthead page.

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1:1 Adducts of Lead(II) Thiocyanate with 1,10-Phenanthroline and 2,2′:6′,2″-Terpyridine[†]

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The chemistry of polypyridyl and related aza-aromatic ligands is currently of considerable interest, particularly as knowledge

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[†] Lewis-Base Adducts of Lead(II) Compounds. 5. Part 4: ref 8.

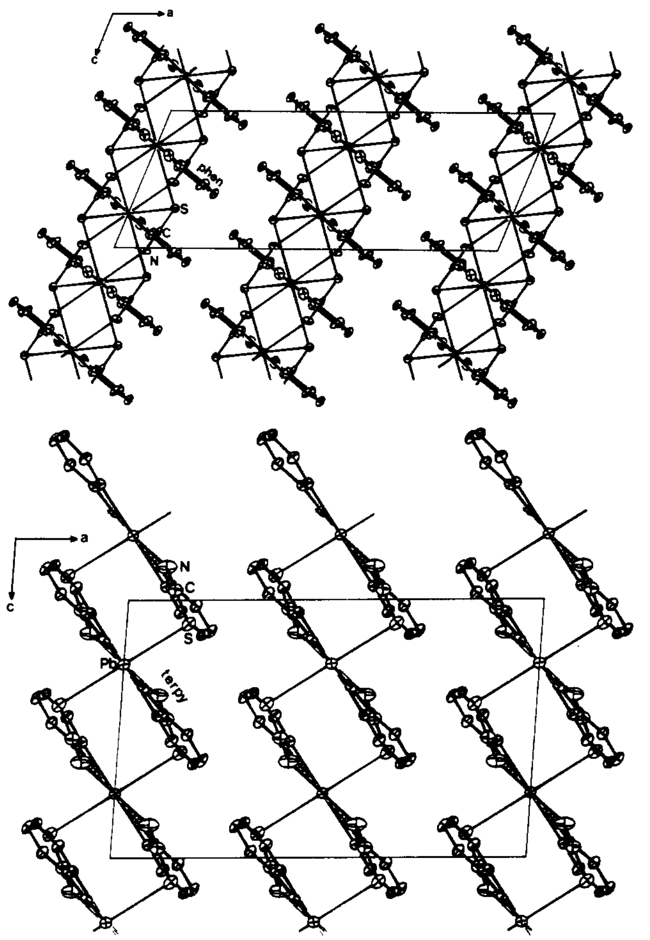

Figure 1. Unit cell contents of (a, top) **1** and (b, bottom) **2**, projected down *b* in each case. 20% thermal ellipsoids are shown for the non-hydrogen atoms in each case.

of the properties of the higher oligomers has expanded and the significant differences between their properties has become apparent.[1] As part of our program of systematic characterization of the structural coordination chemistry of lead(II), we have examined various complexes of lead(II) thiocyanate with 1,10-phenanthroline (phen) and 2,2′:6′,2″-terpyridine (terpy). Complexes of lead with the latter ligand are little known, the earliest work in fact concerning complexes of lead(IV),[2] so that aspects of both the metal ion and the ligand structures in their complexes require definition. We report and compare herein the synthesis and structural characterization of 1:1 adducts of lead(II) thiocyanate with both phen[3] and terpy.

Recrystallization of 1:1 molar ratios of lead(II) thiocyanate with 1,10-phenanthroline (phen) and 2,2′:6′,2″-terpyridine (terpy) (typically on a scale of 0.1 g of $Pb(SCN)_2$, 0.3 mmol) by slow cooling of solutions in the minimum hot water (~100 mL) yields deposits of colorless and yellow needles (needle axes *c*), respectively. (anal. Calcd for $C_{14}H_8N_4PbS_2$ (**1**): C, 33.4; H, 1.6; N, 11.1. Found: C, 33.4; H, 1.5; N, 11.1. Mp: 247 °C. Calcd for $C_{17}H_{11}N_5PbS_2$ (**2**): C, 36.7; H, 2.0; N, 12.6, S, 11.5. Found: C, 36.5; H, 1.9; N, 12.5; S, 11.6. Mp: 274 °C). Single-crystal X-ray structural characterization is consistent with the stoichiometry and connectivity demanded by the 1:1 formulations $(SCN)_2Pb \cdot phen$ and $(SCN)_2Pb \cdot terpy$.

Unique data sets were measured at ~295 K within $2\theta_{max}$ = 50 (**1**), 60° (**2**) by using a Syntex $P2_1$ four-circle diffractometer (conventional $2\theta/\theta$ scan mode; monochromatic Mo Kα radiation). *N* independent reflections were measured, N_o with $I > 3\sigma(I)$ being considered "observed" and used in the full-matrix least-squares refinements (minimizing $\sum w\Delta^2$) after analytical absorption corrections and solution of the structures by heavy-atom methods.

Table I. Crystallographic Data for **1** and **2**[a]

	1	**2**
formula	$C_{14}H_8N_4PbS_2$	$C_{17}H_{11}N_5PbS_2$
M_r	503.5	556.6
a, Å	17.529 (4)	16.145 (10)
b, Å	13.390 (3)	10.820 (4)
c, Å	6.783 (2)	10.010 (5)
β, deg	112.26 (2)	94.27 (5)
V, Å^3	1473.2 (6)	1744 (2)
ρ_{calc}, g·cm^{-3} (*Z*)	2.27 (4)	2.12 (4)
μ_{Mo}, cm^{-1}	113	96
T: min, max	0.50, 0.55	0.25, 0.44
N, N_o	1298, 1230	2546, 1979
R, R_w	0.039, 0.046	0.040, 0.033

[a] Both compounds are monoclinic, space group *C*2/*c* (C^6_{2h}, No. 15); λ = 0.71069 Å, *T* ~ 295 K.

Table II. Non-Hydrogen Atom Coordinates of **1**

atom	*x*	*y*	*z*
Pb	0	0.14100 (6)	$^1/_4$
		Thiocyanate Ligand	
S	0.1160 (2)	0.0614 (3)	0.7112 (6)
C	0.0979 (7)	0.1368 (11)	0.8862 (23)
N	0.0846 (8)	0.1849 (9)	1.0186 (18)
		Phenanthroline Ligand	
N	0.0779 (6)	0.3003 (7)	0.4012 (17)
C(1)	0.1573 (8)	0.3012 (11)	0.5383 (23)
C(2)	0.2028 (8)	0.3886 (12)	0.6010 (23)
C(3)	0.1682 (9)	0.4791 (12)	0.5305 (24)
C(4)	0.0837 (9)	0.4817 (10)	0.3898 (23)
C(5)	0.0408 (7)	0.3884 (9)	0.3214 (20)
C(6)	0.0424 (9)	0.5711 (11)	0.3224 (27)

Table III. Non-Hydrogen Atom Coordinates of **2**

atom	*x*	*y*	*z*
Pb	0	0.15439 (4)	$^1/_4$
		Thiocyanate Ligand	
S	0.1494 (2)	0.1937 (2)	0.0944 (3)
C	0.1119 (7)	0.1170 (8)	−0.0367 (9)
N	0.0865 (7)	0.0651 (7)	−0.1282 (8)
		Terpyridyl Ligand	
N(1)	0	0.3907 (7)	$^1/_4$
C(1)	0.0485 (5)	0.4545 (7)	0.3387 (7)
C(2)	0.0501 (5)	0.5841 (7)	0.3411 (8)
C(3)	0	0.6492 (10)	$^1/_4$
N(11)	0.0873 (4)	0.2598 (5)	0.4498 (6)
C(11)	0.1025 (5)	0.3839 (7)	0.4402 (8)
C(12)	0.1642 (6)	0.4414 (7)	0.5243 (9)
C(13)	0.2046 (5)	0.3722 (8)	0.6237 (9)
C(14)	0.1848 (6)	0.2484 (8)	0.6364 (8)
C(15)	0.1277 (6)	0.1968 (7)	0.5482 (8)

Anisotropic thermal parameters were refined for the non-hydrogen atoms; $(x, y, z, U_{iso})_H$ were included constrained at estimated values. Conventional residuals *R*, *R*′ on |*F*| are quoted. Statistical reflection weights were used, derived from $\sigma^2(I) = \sigma^2(I_{diff}) + 0.0005\sigma^4(I_{diff})$. Neutral-atom complex scattering factors were used;[4] computation used the XTAL 83 program system[5] implemented by S. R. Hall on a Perkin-Elmer 3241 computer. Pertinent results are given in Tables I–V and Figures 1 and 2; the latter define atom numbering. In both cases the centrosymmetric space group was adopted, giving smooth refinement with

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Table IV. Lead Environment of **1**[a]

atom	r	S	N^{i}	S^{ii}	N^{iii}	$N_{phen}{}^{ii}$	S^{iv}	S^{v}
N_{phen}	2.530 (10)	80.8 (2)	73.2 (4)	136.3 (3)	84.7 (4)	65.1 (3)	150.7 (3)	116.7 (3)
S	3.199 (3)		111.7 (2)	141.1 (1)	77.4 (2)	136.3 (3)	80.7 (1)	68.8 (1)
N^{i}	2.602 (15)			77.4 (2)	153.9 (4)	84.7 (4)	135.2 (3)	69.2 (3)
S^{v}	3.457 (4)			68.8 (1)	69.2 (3)	116.7 (3)		76.7 (1)

[a] Entries in the second column, r, are metal–ligand distances (Å). Other entries are the angles (deg) subtended by the atoms at the head of the relevant row and column. N_{phen} is the phenanthroline nitrogen. Transformation of the asymmetric unit: (i) $(x, y, z - 1)$; (ii) $(\bar{x}, y, {}^{1}/_{2} - z)$; (iii) $(\bar{x}, y, \bar{z} + 1{}^{1}/_{2})$; (iv) $(\bar{x}, \bar{y}, 1 - z)$; (v) $(x, \bar{y}, z - {}^{1}/_{2})$. For the thiocyanate, C–N,S distances are 1.20 (2) and 1.68 (2) Å; S–C–N angle is 175 (1)°; C^{i}–N^{i}–Pb angle is 130 (1)°. C–S–Pb,Pb$(\bar{x}, \bar{y}, 1 - z)$ angles are 105.7 (5) and 98.3 (5)°. Pb–S–Pb$(\bar{x}, \bar{y}, 1 - z)$ angle is 99.3 (1)°.

Table V. Lead Environment of **2**[a]

atom	r_{Pb-X}	N^{i}	N(1)	N(11)	S^{ii}	N^{iii}	$N(11)^{iii}$
S	2.998 (3)	105.8 (2)	81.84 (5)	85.8 (2)	163.68 (7)	87.4 (2)	87.1 (2)
N^{i}	2.970 (8)		143.1 (2)	150.6 (2)	87.4 (2)	73.8 (2)	79.9 (2)
N(1)	2.557 (8)			64.2 (1)	81.84 (5)	143.1 (2)	64.2 (1)
N(11)	2.621 (6)				87.1 (2)	79.9 (2)	128.4 (2)

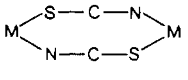
[a] r_{Pb-X} (Å) is the metal–ligand distance. Other entries are the angles subtended at the lead by the relevant atoms at the head of the row and column. Transformation of the asymmetric unit: (i) $(\bar{x}, \bar{y}, \bar{z})$; (ii) $(\bar{x}, y, {}^{1}/_{2} - z)$; (iii) $(x, \bar{y}, {}^{1}/_{2} + z)$. For the thiocyanate, C–S,N distances are 1.631 (9) and 1.126 (12) Å; Pb–S–C, S–C–N, and C–N–Pb^{i} angles are 94.6 (4), 179.1 (9), and 149.9 (7)°.

no anomalies (possible exception: a somewhat enlarged thermal ellipsoid for N in **2** (Figures 1 and 2)).

The dispositions of the two complexes within their respective unit cells is shown in Figure 1, wherein it is clear that both take the aspect of infinite one-dimensional polymers disposed along *c*; in both cases PbL (L = phen, terpy) moieties lie on 2-fold crystallographic axes, so that only half of each ligand is independent. The PbL units are linked by bridging SCN units, one SCN being crystallographically independent in each structure. In both structures successive elements of the polymer are generated by inversion operations (Figure 2), the lead atoms of the polymer strands lying in the *bc* planes. We now consider more detailed aspects individually.

1:1 Adduct $Pb(SCN)_2$·phen (1). The lead atoms are eight-coordinate, PbS_4N_4; two of the coordination sites are occupied by the nitrogen atoms of bidentate phenanthroline, the halves of which are symmetry related by the 2-fold axis that passes through the lead and the midpoints of the C(5)–C(5), C(6)–C(6) bonds; the four nitrogen atoms are clustered about one pole of the symmetry axis, with the four sulfur atoms about its opposite. Away from the phenanthroline, two coordination sites on the other side of the lead atom are occupied by a pair of thiocyanate S atoms; these bridge the lead atom to the preceding and succeeding lead atoms with *y* coordinate of opposite sign by way of centrosymmetric PbS_2Pb units. The other bridging function of the sulfur occupies a pair of symmetry-related sites, quasi-equatorial to the 2-fold axis, which, utilizing the full length of the thiocyanate ligand, bridge through S and N to successive lead atoms of similar *y* coordinate in the other pair of quasi-equatorial sites; it may be noted that this Pb···Pb···Pb array forms an axis through the lead atoms normal to the crystallographic 2-fold axis and that this pair of rectangularly intersecting axes in the projection of Figure 2a in the plane of the paper lie normal to a quasi-4-fold propellor axis in the coordination sphere. Unusually, because of the constraints of the polymer, the nitrogen atom coordination is well removed from linear (Pb–N–C = 130 (1)°); the sulfur environment is pyramidal (Pb–S–Pb = 99.31 (9)°; Pb–S–C = 2 × 98.3 (5)° ($\sum$ = 302.3°). Successive Pb···Pb distances are 5.076 (1) Å. In neither **1** nor **2** is there any suggestion evidenced, e.g., by a large irregularity in the coordination sphere, of a sterically active lone pair; in the present case the maximum angle subtended by any pair of near neighbors in the coordination sphere does not exceed 85°.

1:1 Adduct $Pb(SCN)_2$·terpy (2). The lead atoms are seven-coordinate. The crystallographic 2-fold axis passes through the central terpy N–Pb bond, with bonds on either side from the distant terpy nitrogen atoms to the lead. The terpy coordination is planar tridentate, with two nitrogen atoms from symmetry-related thiocyanato-*N* moieties substantially coplanar (angle sum in the N_5-coordination plane: 362°) and with N–Pb–N angles ranging from 64.2 (1) to 79.9 (2)°. The sulfur ends of a pair of symmetry-related thiocyanate groups coordinate above and below this plane to yield a coordination environment that may reasonably be described as pentagonal bipyramidal: S–Pb–S angle is 163.67 (7)° and S–Pb–N angles range from 81.84 (5) to 87.4 (2)°. The bridging moiety in this structure is the familiar symmetric eight-membered-ring motif, common in thiocyanate structures:[7]



Successive Pb···Pb separations are 6.018 (2) Å.

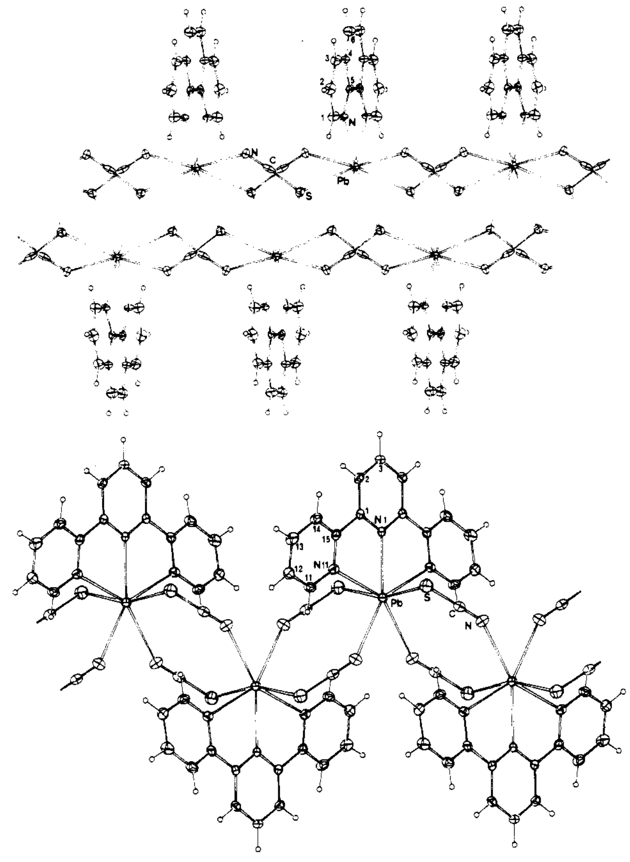


Figure 2. Projections of individual polymer strands of (a, top) **1** and (b, bottom) **2**, normal to the plane of the lead atoms in each case (*bc*). The atom numbering is shown; hydrogen atoms have arbitrary radii of 0.1 Å.

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The aspects of the successive -up-down-up-down- orientation of the ligand bisector relative to the polymer axis in both structures suggests interleaving of the aromatic ring planes from successive strands up *b* (cf. ref 6). The increased successive Pb$\cdots$Pb separation on passing from **1** to **2** is accompanied by increased twist of the ligand about its 2-fold axis so that it is more sharply inclined to the polymer axis, enabling interplanar spacings to remain substantially constant at typical charge-transfer distances. It is of interest that, while successive "up-down" lead atoms in **2** are bridged in an eight-membered ring (note that the thiocyanate ligands are substantially parallel to the terpy in the projections of Figure 2, with bridges to neighboring lead atoms by Pb-S-C angles of 94.6 (4)°), in **1**, successive lead atoms are bridged at the shorter distance by PbS$_2$Pb four-membered rings, while the other bridging functionality of the sulfur enables a leap to the subsequent lead atom of similar disposition: Pb(up)-S-C-N-Pb(up). The subtlety of factors influencing thiocyanate coordination modes is well-known[7] and well-illustrated by the present and related[8] studies.

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Supplementary Material Available: Tables Sup-1-Sup-7, listing crystal and refinement data, thermal parameters, derived hydrogen atom parameters, and phenanthroline and terpyridyl geometries (6 pages); tables of observed and calculated structure factor amplitudes (13 pages). Ordering information is given on any current masthead page.

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Resonance Raman Spectra and Electrochemistry of Mononuclear and Dinuclear (Bis(pyridinyl)triazolato)ruthenium Compounds

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Recently, the synthesis and properties of mononuclear and dinuclear Ru(bpy)$_2$ compounds containing bpt have been reported[2a] (bpy = 2,2'-bipyridine; Hbpt = 3,5-bis(pyridin-2-yl)-1,2,4-triazole; see Figure 1). The bpt anion in the mononuclear compound is coordinated via N1 of the triazole ring and a pyridine ring to the ruthenium ion; in [(Ru(bpy)$_2$)$_2$(bpt)]$^{3+}$, the second Ru(bpy)$_2$ moiety is bound via N4 of the triazole ring and the second pyridine ring.[2a,b] The properties of the dinuclear system are unusual since a rather extensive electron delocalization in the mixed-valence system has been observed. Furthermore, the dinuclear compound emits at room temperature.[2a] Resonance Raman (rR) spectroscopy has often been used to investigate the origin of electronic absorption bands.[3] With the use of this technique, extensive information concerning the electronic structures of various compounds has been obtained.[3] If the observed MLCT (metal to ligand charge transfer) band is due to both Ru → π*(bpy) and Ru → π*(bpt) transitions, then a distinct wavelength dependence in the rR spectra should be manifested within the range of the observed transition. On the other hand, if the absorption band would be caused only by Ru → π*(bpy) transitions, then in all cases the same rR spectra should be observed.

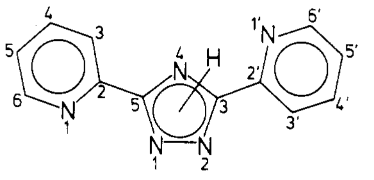

Figure 1. Structural formula of 3,5-bis(pyridin-2-yl)-1,2,4-triazole (Hbpt).

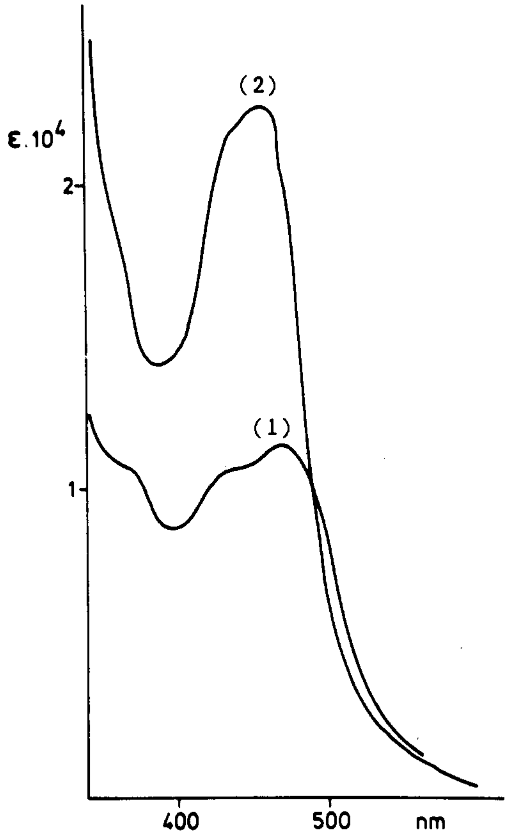

Figure 2. Absorption spectra of [Ru(bpy)$_2$(bpt)]$^+$ (cation of **1**) and [(Ru(bpy)$_2$)$_2$(bpt)]$^{3+}$ (cation of **2**). All compounds were measured in ethanol with a concentration of about 10^{-4} mol/L.

Pyrazoles, imidazoles, and triazoles are known to have high-lying π* orbitals.[4,5] It is therefore of interest to study whether

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