Lewis-Base Adducts of Lead(II) Compounds. Part 4.[1] Novel Isomeric Dimers of Lead(II) Thiocyanate–1,10-Phenanthroline(1/2). Crystal Structure Determinations *

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The 1 : 2 adduct of lead(II) thiocyanate–1,10-phenanthroline has been shown to crystallise as two distinct polymorphs, monoclinic and triclinic. Single-crystal *X*-ray structure determinations show that in both forms the complexes exist as discrete dimers, all lead environments being seven-co-ordinate. The lead environment in all cases comprises a pair of bidentate phenanthroline ligands, unidentate N-thiocyanate, and a pair of bridging thiocyanate ligands, one with bridging sulphur and one bridging through the terminal atoms. In the monoclinic form, *C*2/*c*, the dimer has crystallographically imposed two-fold symmetry with the N,S-bridging thiocyanate disordered about that axis; this ligand in the triclinic form is fully ordered, with ligand rearrangement about one of the lead atoms so that the dimer symmetry is more nearly inversion rather than two-fold.

Despite its high abundance for a heavy element, its industrial importance, and its well known toxicity,[2] lead has not been extensively investigated through structural studies of its compounds, except in respect of its relevance in the analysis of a small number of specific issues such as the stereochemical activity or otherwise of the lead(II) lone pair[3] or the action of Pb^{II} in template synthesis of macrocyclic ligands.[4] The co-ordination chemistry of Pb (particularly Pb^{II}) is in fact very extensive[5] and even the limited extant range of structural studies of lead(II) complexes has revealed a remarkable variety of co-ordination numbers and stereochemistry. In the present work, we describe the structures of two forms of the complex of stoicheiometry $Pb(phen)_2(NCS)_2$ (phen = 1,10-phenanthroline) in which an unusual form of stereoisomerism is displayed. In part, this work was undertaken in an effort to characterise the reported[6] complex $Pb(phen)_3(NCS)_2$ but, in the presence of 2 mol of thiocyanate ion, we have not been able to co-ordinate more than 2 mol of phen to Pb^{II}.

Experimental

Synthesis.—Lead(II) thiocyanate was obtained as small, white crystals by addition of a twice molar quantity of sodium thiocyanate to a hot solution of lead(II) nitrate in water. (Note that the compound is photosensitive and begins to turn yellow within a few days.) 1,10-Phenanthroline monohydrate was used as purchased from Fluka.

Lead(II) *thiocyanate*–1,10-*phenanthroline*(1/2), α(*monoclinic*) *isomer.* Lead(II) thiocyanate (0.10 g, 0.3 mmol) and 1,10-phenanthroline monohydrate (0.12 g, 0.6 mmol) were dissolved in the minimum volume of boiling water (*ca.* 100 cm^3) and the final solution allowed to stand to cool slowly to room temperature. Fine, colourless needles of the 1 : 2 adduct deposited (m.p. 223 °C). Recrystallisation from hot water changed neither the composition nor the melting point of this material (Found: C, 45.7; H, 2.6; N, 12.3. Calc. for $C_{26}H_{16}N_6PbS_2$: C, 45.7; H, 2.4; N, 12.3%).

In our hands, the same material was obtained in attempting to follow the literature procedure[6] for the preparation of $Pb(phen)_3(NCS)_2$. Note that in this procedure the actual molar ratio of Pb^{II} : phen is 1 : 1.

Lead(II) *thiocyanate*–1,10-*phenanthroline*(1/2), β(*triclinic*) *isomer.* Lead(II) thiocyanate (0.10 g) and 1,10-phenanthroline monohydrate (0.18 g, 0.9 mmol) were dissolved in boiling water (*ca.* 150 cm^3). On cooling, small fine white needles of a 1 : 2 adduct deposited, m.p. 186 °C (Found: C, 46.4; H, 2.7; N, 12.3%).

Structure Determinations.—Unique data sets were measured at *ca.* 295 K within the given $2\theta_{max.}$ limit using a Syntex $P2_1$ four-circle diffractometer operating in conventional 2θ–θ scan mode, and with monochromatic Mo-K_α radiation source (λ = 0.710 69 Å). *N* Independent reflections were measured, N_o with $I > n\sigma(I)$ being considered 'observed' and used in the large-block least-squares refinements after gaussian absorption corrections and solution of the structures by vector methods. Anisotropic thermal parameters were refined for the non-hydrogen atoms; (x,y,z,U_{iso}) were included constrained at estimated values. Conventional residuals on $|F|$, *R*, *R′* at convergence are given; statistical reflection weights derived from $\sigma^2(I) = \sigma^2(I_{diff}) + 0.000n_w\sigma^4(I_{diff})$ were employed. Neutral atom complex scattering factors were employed;[7] computation used the XTAL program system,[8] implemented by S. R. Hall. Pertinent results are given in the Tables and Figure, the latter showing the non-hydrogen atom-numbering schemes and thermal envelopes at the 20% probability level for the non-hydrogen atoms; hydrogen atoms have arbitrary radii of 0.1 Å.

Crystal data. α-$C_{26}H_{16}N_6PbS_2$, *M* = 683.8, monoclinic, space group *C*2/*c* (C^6_{2h}, no. 15), *a* = 9.361(3), *b* = 18.790(5), *c* = 28.119(6) Å, β = 101.81(2)°, *U* = 4 841(2) $Å^3$, *Z* = 8, D_c = 1.88 g cm^{-3}, *F*(000) = 2 624, μ_{Mo} = 69 cm^{-1}, specimen, plate 0.26 × 0.06 × 0.25 mm, $A^*_{min.,max.}$ = 1.33, 4.55, $2\theta_{max.}$ = 50°, *N* = 4 217, N_o [2σ(*I*)] = 2 872, *R* = 0.055, *R′* = 0.036 (n_w = 5).

β-$C_{26}H_{16}N_6PbS_2$, triclinic, space group $P\bar{1}$ (C^1_i, no. 2), *a* = 18.64(3), *b* = 15.55(2), *c* = 9.097(8) Å, α = 96.52(8), β = 92.49(8), γ = 113.14(9)°, *U* = 2 399(4) $Å^3$, *Z* = 4, D_c = 1.89 g cm^{-3}, *F*(000) = 1 312, μ_{Mo} = 69 cm^{-1}, specimen, needle 0.03 × 0.07 × 0.30 mm, $A^*_{min.,max.}$ 1.14, 1.78, $2\theta_{max.}$ = 45°, *N* = 5 723, N_o [3σ(*I*)] = 3 006, *R* = 0.049, *R′* = 0.049 (n_w = 7).

Abnormal features. α *Form.* One of the thiocyanate species (c) lies disordered about the two-fold axis (or there is an unresolved small lower-symmetry perturbation on the assumed

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* *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1989, Issue 1, pp. xvii—xx.

Table 1. Non-hydrogen atom co-ordinates

	α			Unprimed section β			Primed section β		
Atom	*x*	*y*	*z*	*x*	*y*	*z*	*x*	*y*	*z*
Pb	0.473 20(6)	0.337 39(3)	0.140 07(2)	0.330 10(5)	0.223 94(6)	0.318 75(10)	0.192 29(6)	−0.211 75(6)	0.267 88(10)
Thiocyanate group									
S(a)	$\frac{1}{2}$	0.382 3(3)	$\frac{1}{4}$	0.167 8(4)	0.325 7(5)	0.688 8(7)			
C(a)	$\frac{1}{2}$	0.480 5(13)	$\frac{1}{4}$	0.198(1)	0.298(1)	0.531(2)			
N(a)	$\frac{1}{2}$	0.535 9(11)	$\frac{1}{4}$	0.219(1)	0.286(1)	0.414(2)			
S(b)	0.097 1(5)	0.531 2(3)	0.087 2(2)	0.392 2(4)	−0.058 0(5)	0.217 3(8)	0.309 7(5)	−0.334 8(6)	−0.119 1(10)
C(b)	0.241 2(18)	0.491 7(8)	0.100 7(4)	0.406(1)	0.041(2)	0.317(2)	0.292(1)	−0.316(2)	0.060(3)
N(b)	0.365 8(15)	0.461 6(7)	0.107 6(4)	0.416(1)	0.114(1)	0.388(2)	0.278(1)	−0.310(2)	0.176(3)
S(c)	0.420 0(8)	0.199 3(4)	0.209 3(2)	0.218 7(4)	0.002 2(4)	0.296 7(7)			
C(c)	$\frac{1}{2}$	0.205 2(12)	$\frac{1}{4}$	0.130(1)	−0.016(2)	0.265(2)			
N(c)				0.065(1)	−0.029(2)	0.241(3)			
Phenanthroline ligands									
N(1a)	0.693 9(11)	0.417 7(6)	0.159 9(3)	0.235 3(8)	0.181(1)	0.093(2)	0.265 1(10)	−0.172(1)	0.508(2)
C(1a1)	0.677 2(15)	0.488 8(9)	0.163 0(5)	0.160(1)	0.166(1)	0.092(2)	0.342(2)	−0.160(2)	0.528(3)
C(1a2)	0.784 4(18)	0.536 9(11)	0.177 5(6)	0.105(1)	0.134(1)	−0.031(2)	0.389(1)	−0.126(1)	0.667(3)
C(1a3)	0.924 5(20)	0.509 1(9)	0.187 9(5)	0.127(1)	0.113(1)	−0.171(2)	0.354(1)	−0.103(2)	0.785(3)
C(1a4)	0.952 6(14)	0.434 3(10)	0.186 2(4)	0.206(1)	0.127(1)	−0.172(2)	0.280(1)	−0.110(1)	0.783(2)
C(1a5)	0.824 8(13)	0.385 9(8)	0.171 2(4)	0.259(1)	0.159(1)	−0.043(2)	0.237(1)	−0.144(1)	0.637(2)
C(1a6)	1.095 2(15)	0.396 4(10)	0.199 4(5)	0.235(1)	0.104(1)	−0.318(2)	0.243(1)	−0.087(2)	0.899(2)
C(1b6)	1.102 8(13)	0.320 5(10)	0.198 5(4)	0.309(1)	0.111(2)	−0.317(2)	0.170(1)	−0.092(1)	0.884(2)
C(1b5)	0.833 0(12)	0.308 8(8)	0.170 6(4)	0.336(1)	0.165(2)	−0.048(2)	0.157(1)	−0.151(1)	0.620(2)
C(1b4)	0.974 8(14)	0.271 2(10)	0.186 2(4)	0.362(1)	0.141(1)	−0.190(2)	0.124(1)	−0.125(1)	0.744(2)
C(1b3)	0.973 5(22)	0.194 7(9)	0.186 4(5)	0.438(1)	0.148(2)	−0.191(2)	0.049(1)	−0.126(1)	0.723(2)
C(1b2)	0.843 6(17)	0.160 5(10)	0.173 0(5)	0.485(1)	0.176(1)	−0.063(2)	0.009(1)	−0.158(1)	0.579(2)
C(1b1)	0.717 6(15)	0.200 3(8)	0.157 3(5)	0.455(1)	0.200(2)	0.068(2)	0.042(1)	−0.189(1)	0.464(2)
N(1b)	0.714 0(10)	0.269 1(6)	0.157 3(3)	0.382 2(9)	0.194(1)	0.074(2)	0.115 3(8)	−0.181(1)	0.485(2)
N(2a)	0.553 9(11)	0.345 9(7)	0.055 0(3)	0.368 4(9)	0.387(1)	0.218(2)	0.133 1(10)	−0.374(1)	0.356(2)
C(2a1)	0.620 3(16)	0.404 5(9)	0.044 5(5)	0.315(1)	0.402(2)	0.140(3)	0.176(1)	−0.397(1)	0.450(3)
C(2a2)	0.678 7(19)	0.408 2(10)	0.002 3(5)	0.336(1)	0.486(2)	0.075(3)	0.155(1)	−0.484(2)	0.499(3)
C(2a3)	0.654 4(17)	0.352 8(10)	−0.030 2(5)	0.414(1)	0.552(1)	0.090(3)	0.085(1)	−0.550(2)	0.440(3)
C(2a4)	0.577 1(14)	0.291 6(8)	−0.021 2(4)	0.469(1)	0.534(1)	0.175(3)	0.033(1)	−0.535(1)	0.342(2)
C(2a5)	0.530 6(13)	0.290 2(7)	0.022 1(4)	0.446(1)	0.448(1)	0.241(2)	0.061(1)	−0.441(1)	0.298(3)
C(2a6)	0.547 1(16)	0.235 1(9)	−0.053 9(4)	0.548(1)	0.600(2)	0.198(3)	−0.039(1)	−0.596(2)	0.266(3)
C(2b6)	0.471 8(15)	0.180 0(10)	−0.046 0(4)	0.601(1)	0.582(2)	0.280(3)	−0.090(1)	−0.582(2)	0.174(3)
C(2b5)	0.449 0(13)	0.231 6(7)	0.032 9(4)	0.501(1)	0.429(1)	0.331(2)	0.016(1)	−0.414(1)	0.201(2)
C(2b4)	0.416 2(13)	0.177 3(8)	−0.002 3(4)	0.579(1)	0.497(2)	0.350(2)	−0.055(1)	−0.483(2)	0.142(2)
C(2b3)	0.330 6(16)	0.119 6(9)	0.008 3(5)	0.634(1)	0.478(2)	0.436(3)	−0.103(1)	−0.461(1)	0.046(3)
C(2b2)	0.265 3(18)	0.119 4(9)	0.050 5(5)	0.610(1)	0.395(2)	0.500(3)	−0.078(1)	−0.373(1)	0.004(3)
C(2b1)	0.309 4(15)	0.177 4(9)	0.081 4(4)	0.534(1)	0.334(2)	0.470(3)	−0.001(2)	−0.307(2)	0.070(3)
N(2b)	0.397 1(11)	0.230 1(6)	0.074 5(3)	0.479 8(11)	0.349(1)	0.385(2)	0.045(1)	−0.325(1)	0.167(2)

space group). It was modelled in terms of fractionally populated sulphur (population refined to a value not greatly different from the statistical expectation for 0.5S/0.5N) and the central carbon on the axis, albeit with a predictably unrealistic ellipsoid. Abnormal thermal motion was also observed in thiocyanate (a), possibly indicative of concerted off-axis perturbations, and at the phenanthroline periphery is also high.

β *Form.* The data from the small specimen were generally weak and would not support stable refinement of anisotropic thermal parameter forms for all atoms, in consequence of which some were restored to the isotropic mode.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates, thermal parameters, and remaining bond distances and angles.

Discussion

The adducts formed between Pb(NCS)$_2$ and 1,10-phenanthroline are highly water-insoluble, yet easily crystallised materials which may thus be rather useful materials for the gravimetric estimation of lead.[6] Such analysis of course requires that the stoicheiometry of the precipitated solid be well established and it is therefore important to confirm the composition of the compound reported[6] as Pb(phen)$_3$(NCS)$_2$. We have found, however, that the compound prepared under the exact conditions described[6] consistently gave analyses indicative of the formation of a bis(1,10-phenanthroline) adduct only. Indeed, repeated efforts to crystallise lead(II) thiocyanate from solutions containing molar ratios of phen to Pb^{II} much greater than 2:1 consistently yielded material of similar stoicheiometry. They did, nonetheless, provide a material with the same melting point as that attributed to Pb(phen)$_3$(NCS)$_2$. While the mechanism whereby two physically distinct materials of identical chemical composition may be reproducibly obtained from media of quite similar composition remains obscure, our structural studies have now shown that a genuine, novel isomerism exists in the Pb(phen)$_2$(NCS)$_2$ system.

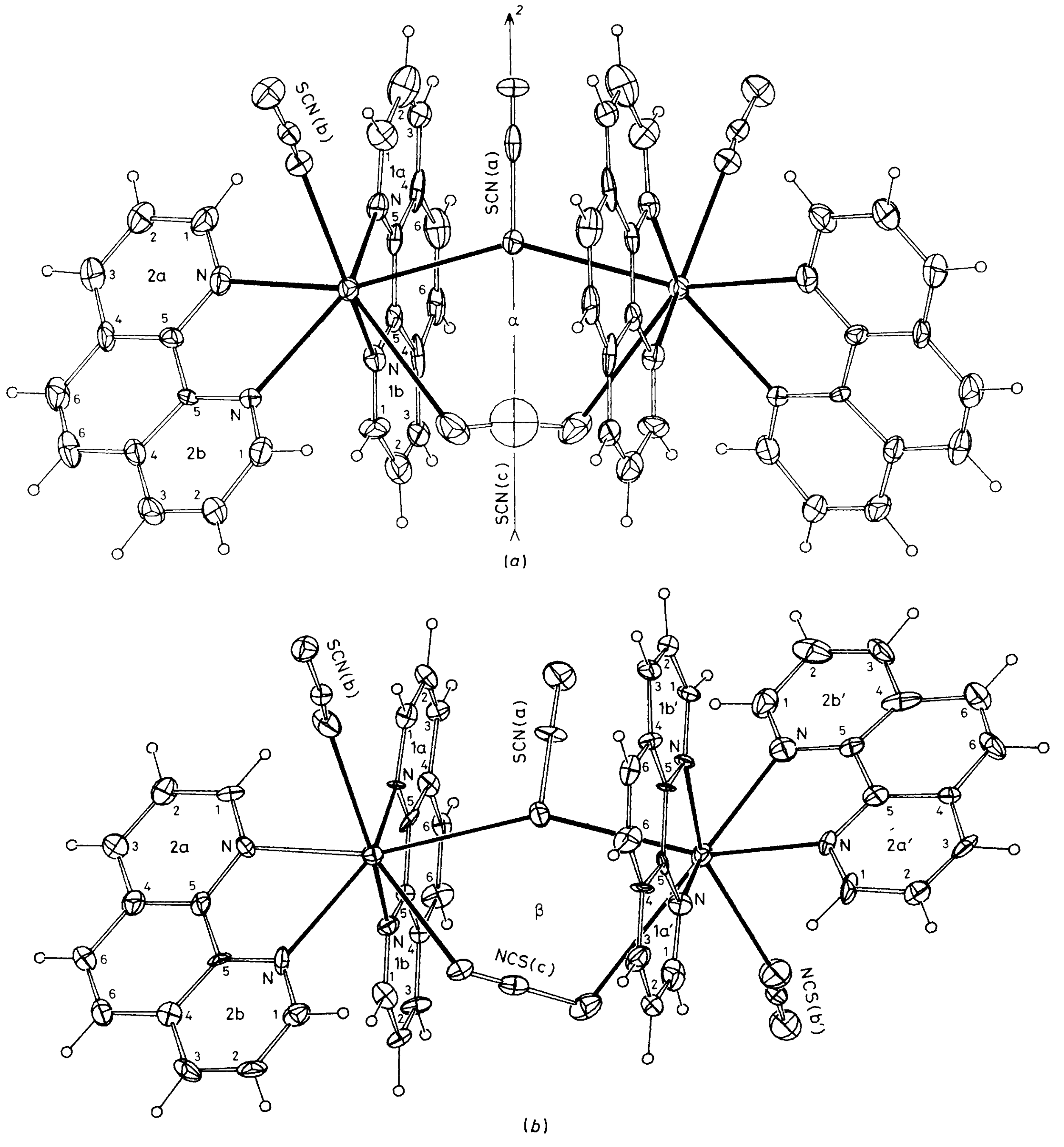

Figure. (*a*) A projection of the dimer of the α form, normal to the plane of the *2* axis and the Pb ··· Pb line. 20% Non-hydrogen thermal envelopes are shown together with atom labelling. Hydrogen atoms have arbitrary radii of 0.1 Å. (*b*) The dimer of the β form

α-Lead Thiocyanate–1,10-*Phenanthroline*(1/2).—The results of the structure determination are consistent with the above stoicheiometry and connectivity, one formula unit comprising the asymmetric unit of the structure. This unit, however, is disposed close to a crystallographic *2* axis and, with its image, comprises a binuclear species (Figure). The two lead atoms of the dimer are seven-co-ordinate, with five of the co-ordination sites being occupied by a pair of bidentate 'phen' moieties, together with a unidentate N-bonded thiocyanate. The remaining pair of sites is occupied by bridging thiocyanate moieties which link the two lead atoms across the *2* axis. One of the thiocyanate groups lies on that axis, with the sulphur atom above performing the bridging function; the sulphur environment is, in consequence, planar [Pb–S–Pb, 149.0(2); Pb–S–C, 2 × 105.5(1)°; Σ 360°] without excessive amplitude in its thermal ellipsoid suggestive of disorder, although the associated C,N thermal motion is less well behaved (see above and Figure). The other bridging thiocyanate group in the present space group is modelled as a disordered species lying normal to the *2* axis, with the carbon atom on that axis and a terminal composite N,S off-axis pseudo-atom. Sulphur and nitrogen at either end must, regardless of the large-amplitude thermal envelopes encompassing the disorder, co-ordinate at an angle well removed from straight [Pb–'S(3)'–'C', 110(1)°] in spite of the need to regard the actual value of this angle circumspectly.

Table 2. Lead environments. $r_{\mathrm{Pb-X}}$ is the metal–ligand distance (Å). Other entries are the angles (°) subtended at the lead atom by the relevant atoms at the head of the row and column. Entries, in order, are for α, β, β′ lead atoms

Atom	$r_{\mathrm{Pb-X}}$	N(1b)	N(2a)	N(2b)	N(b)	S(a) [S(c)[a]]	S,N(c) [S(a)[a]]
N(1a)	2.53(1) 2.50(2) 2.41(2)	66.9(3) 64.5(6) 66.1(6)	78.0(3) 77.8(5) 81.3(5)	132.8(3) 133.0(5) 133.4(6)	77.5(4) 77.0(6) 88.7(7)	74.2(2) 72.5(4) 73.6(4)	123.2(2) 123.3(5) [86.1(3)]
N(1b)	2.55(1) 2.53(2) 2.60(2)		78.4(3) 77.8(6) 77.5(6)	81.7(3) 81.5(6) 78.1(5)	140.5(4) 137.1(6) 143.1(7)	93.3(2) 90.7(4) 124.3(3)	74.3(3) 77.1(6) [73.0(4)]
N(2a)	2.66(1) 2.63(2) 2.56(2)			61.2(4) 63.5(6) 62.0(6)	78.1(4) 76.3(6) 72.1(6)	152.0(3) 150.3(4) 132.4(5)	132.4(3) 133.6(5) [150.6(4)]
N(2b)	2.73(1) 2.69(2) 2.67(2)				113.2(3) 115.5(6) 104.7(6)	144.6(2) 142.4(5) 152.8(4)	76.7(3) 74.6(5) [111.6(5)]
N(b)	2.63(1) 2.74(2) 2.71(3)					92.9(3) 95.2(4) 67.6(4)	143.1(3) 143.7(6) [134.3(4)]
S(a) [S(c)[a]]	3.165(2) 3.228(6) [3.635(7)]						68.3(2) 67.8(3) [67.3(2)]
S,N(c) [S(a)[a]]	3.341(8) 2.86(2) [3.145(7)]						

For the thiocyanate groups[b]

Ligand	a	b	c
S–C	1.84(3); 1.58(2)	1.52(2); 1.64(2), *1.69(3)*	1.24(1); 1.61(2)
C–N	1.04(3); 1.15(3)	1.27(2); 1.17(3), *1.10(4)*	— ; 1.19(3)
Pb,*Pb′*–N		2.63(1); 2.74(2), *2.71(3)*	[3.341(8)]; 2.86(2)
Pb,*Pb′*–S	3.165(2); 3.228(6), *3.145(7)*		3.341(8); *3.635(8)*
N–C–S	180(–); 180(2)	173(1); 173(2), *176(2)*	170(2); 179(2)
C–N–Pb,*Pb′*		136(1); 133(2), *121(2)*	— ; 122(2)
C–S–Pb,*Pb′*	105.5(1); 111(1), *96(1)*		110(1); *103.7(8)*
Pb–S–Pb′	149.0(2); 152.0(3)		

[a] β′ atom. [b] α; β. Italicised values are for the primed section in the β form.

Table 3. Geometry of the $(N_2)_2Pb(N)$ moiety in $[Pb(phen)_2(NCS)(O_2NO)]$. The ordering of atoms is that of the top left-hand corner of Table 2; atom numbering is that of ref. 1

Atom	$r_{\mathrm{Pb-X}}$	N(2a)	N(1a)	N(1b)	N
N(2b)	2.50(2)	67.5(4)	86.4(4)	141.2(4)	76.9(4)
N(2a)	2.49(1)		75.4(4)	82.6(4)	135.8(4)
N(1a)	2.53(1)			61.7(4)	77.0(4)
N(1b)	2.60(1)				113.2(4)
N	2.89(1)				

β-*Lead Thiocyanate*–1,10-*Phenanthroline*(1/2).—The results of the structure determination are consistent with the above stoicheiometry and connectivity, but the asymmetric unit of the structure is now two formula units; the two lead atoms are linked to form a dimer superficially similar to that found in the α form but without internal crystallographically imposed exact, or quasi-, symmetry, and describable without disorder.

One lead atom, Pb, has an environment very similar to that of the α form (Table 2), differing grossly only in that the co-ordination site occupied by the disordered bridging thiocyanate group is now occupied by the nitrogen atom of an ordered, similarly bridging thiocyanate group, c; in detail, lead–ligand distances and angles are not non-trivially different. The seven-co-ordinate lead environment may be viewed as a crude pentagonal bipyramid, with the N-co-ordinated thiocyanate and (1b) *trans*; the sum of the angles between the five equatorial ligand atoms is appreciably less than 360°, however [347.3(α), 342.9°(β)]. Atom N(b) leans toward N(1a,2a), leaving an appreciable cavity which may be indicative of a sterically active lone pair.

The other lead atom, Pb′, is also seven-co-ordinate, but co-ordination by way of the sulphur atom of bridging thiocyanate 'c' is more tenuous [Pb–S 3.635(7) Å], and the atom dispositions relative to the incipient *2* axis of the α form have now been permuted, giving rise to a new isomer, differing most conspicuously in the disposition of the N-monodentate thiocyanate group relative to that *2* axis. A very large gap exists in the co-ordination sphere away from the viewer in the Figure. The two lead atom environments, however, are remarkable for the similarity of the common $(phen)_2Pb(NCS)$ arrays (Table 2), a geometry which persists in $[Pb(phen)_2(NCS)(O_2NO)]$, also seven-co-ordinate (Table 3).[1]

Only limited comparisons of the present work with other co-ordination chemistry of $Pb(NCS)_2$ are possible. The general co-ordination chemistry of the ambidentate thiocyanate ion is quite complicated[9,10] and it is not surprising to see several modes of co-ordination to Pb^{II}. In lead(II) thiocyanate itself, for example, a relatively recent structure determination[11] has shown the lead atom to be eight-co-ordinate (4N at 2.69 and 2.78; 4S at 3.00 and 3.14 Å) with crystallographically imposed two-fold symmetry and bridging thiocyanate groups. In its complexes, bridging Pb–S–C–N–Pb modes similar to the present examples are found [*e.g.* in $Pb(NCS)_2(dmso)_2$ (dmso = dimethyl sulphoxide);[10,12] a weak bridging interaction is suggested to be present in a macrocycle derivative[4]], although Pb–N–C in the present β form is remarkable for its 'acuteness' [122(1)°]. Both thiocyanato (Pb–S–C–N) and 'isothiocyanato' (Pb–N–C–S) modes of unidentate co-ordination have been observed, remarkably, in the one complex, presumably in consequence of steric restraints imposed by a $C_{18}H_{36}N_2O_6$ macrobicycle.[13]

Acknowledgements

We gratefully acknowledge partial support of the work by grants from the Australian Research Grant Scheme.

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Received 2nd June 1988; *Paper* 8/02203H