Chemistry of Subvalent Main Group Metals with Dithiolates. Part 2.[1] *X*-Ray Structural, Thermal, and Theoretical Investigations on the Novel One-dimensional Stacking Structure $K_2[Pb\{S_2C{=}C(CN)_2\}_2]\cdot 2H_2O$ †

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The structure of $K_2[Pb\{S_2C{=}C(CN)_2\}_2]\cdot 2H_2O$ has been determined from 673 reflections of a twinned crystal and refined to an *R* factor of 0.094 ($R' = 0.085$). It consists of one-dimensional $[Pb\{S_2C{=}C(CN)_2\}_2]^{2-}$ anions stacked along the crystallographic *b* direction with Pb . . . Pb 4.074 Å and interspersed K^+ cations. The anion has a pyramidal geometry with Pb at the top exhibiting an apparently stereochemically active lone pair. By use of relativistic Hartree–Fock molecular orbital calculations it is shown that the pyramidal geometry is 25 kcal mol^{-1} (104.6 kJ mol^{-1}) more stable than a planar arrangement. Within the stack there is no significant interaction between the anions.

A number of studies have been carried out recently on the structural evidence of the lone-pair effect of subvalent metal cations.[1–6] Burdett and Lin[7] showed that the lone-pair effect in red PbO is a result of a distortion of the CsCl-type structure giving rise to a mixing of the 6*s* orbital of Pb and *p*-type orbitals located on oxygen. On the other hand, PbS crystallizes in an undistorted sodium chloride lattice with the valence electrons of lead residing in the stereochemically inert 6*s* orbital.

The growing interest in stereochemical consequences of the lone-pair effect, and in particular in interactions between subvalent metal cations, led us to carry out a detailed study of thiolates with metal cations in low oxidation states.[1] It is assumed that in several cases a tuning of the lone-pair effect by the thiolate is possible. In order to understand the electronic interactions between metal cations and ligands we have approached the problem using molecular orbital calculations and *X*-ray structural analysis. In a previous work[1] we reported the structures of the $[Pb\{S_2C{=}C(CN)_2\}]$ system. The present paper deals with the first structure containing the complex anion $[Pb\{S_2C{=}C(CN)_2\}_2]^{2-}$.

Experimental

Preparation of $K_2[Pb\{S_2C{=}C(CN)_2\}_2]\cdot 2H_2O$.—A raw product was obtained from stoicheiometric amounts of $K_2[S_2C{=}C(CN)_2]\cdot H_2O$[8] and $Pb(CH_3COO)_2\cdot 3H_2O$ in water. For crystallization the yellow product was dissolved in acetone with traces of water. By gas diffusion of diethyl ether into the solution, needle-shaped crystals of $K_2[Pb\{S_2C{=}C(CN)_2\}_2]\cdot 2H_2O$ were obtained (Found: C, 16.05; H, 0.50; N, 9.20; H_2O, 6.00. Calc. for $C_8H_4K_2N_4O_2PbS_4$: C, 15.95; H, 0.65; N, 9.30; H_2O, 6.00%).

X-Ray Crystal Structure of $K_2[Pb\{S_2C{=}(CN)_2\}_2]\cdot 2H_2O$.—Weissenberg and precession photographs showed a reflection pattern typical for pseudo-merohedric twinned crystals with a [100]-twin axis and systematic extinction *hkl*: $h + k = 2n + 1$.[9] The resolvable reflections and the superimposed ones were obtained for a crystal with size 0.6 × 0.1 × 0.1 mm.

Crystal data. $C_8H_4K_2N_4O_2PbS_4$, $M = 601.80$, monoclinic, space group *C*2, $a = 25.059(4)$, $b = 4.074(1)$, $c = 8.480(2)$ Å, $\beta = 99.2(3)°$, $U = 855(1)$ Å^3, $D_m = 2.29$ g cm^{-3}, $Z = 2$, $D_c = 2.34$ g cm^{-3}, Ag-K_α radiation, $\lambda = 0.5594$ Å, $\mu = 5.92$ mm^{-1}, $F(000) = 552$, $T = 23(2)$ °C.

Structure determination and refinement. Data were collected with a PW 1100 Philips diffractometer using graphite-monochromated Ag-K_α radiation. Lattice parameters were determined from 25 high-indexed reflections with $12 < \theta \leqslant 19°$. A total of 3 448 reflections with $\theta \leqslant 19°$ were collected using ω scan, scan width $(1.50 + 0.20 \tan \theta)°$ with scan speed 0.15° s^{-1}. Three standard reflections were monitored after each 60 reflections and indicated no significant deviations. Merging gave 817 symmetry-independent reflections with 673 having intensities greater than $5.5\sigma(I)$ and were taken as observed. Based on a Patterson synthesis and statistical tests, we chose the space group *C*2.[10,11] By omitting the superimposed reflections (*h*00) the full model of the structure was developed during several Fourier and least-square cycles. By using all reflections during the refinement, $\Sigma w(|F_o| - |F_c|)^2$ was minimized to $R = 0.094$ and $R' = 0.085$ respectively. Only K and Pb atoms were refined with anisotropic thermal parameters. The positions of the hydrogen atoms were obtained from a Fourier synthesis and refined using the constraints O–H 0.96(3) and H $\cdots$ H = 1.56(3) Å with a common isotropic thermal parameter. A weighting scheme $w = 7.784[\sigma^2(F) + 7 \times 10^{-5}F^2]^{-1}$ was employed during the last refinement and 58 parameters were refined. Atomic scattering and dispersion factors for neutral atoms were used.[12,13] A CYBER 854 computer system at Regionales Rechenzentrum der Universität Erlangen-Nürnberg and the SHELX 76 system[10] were used for all crystallographic calculations.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates and thermal parameters.

Thermal Investigations.—Differential thermal analysis–thermal gravimetry (d.t.a.–t.g.) measurements were performed with a STA 429 Netzsch instrument. A linear temperature scan was applied from 20 to 500 °C with heating rates of 2 and 5 °C min^{-1}. Standards were Al_2O_3 and $Ca(C_2O_4)\cdot 2H_2O$. During all operations the samples were handled under nitrogen. The temperature-dependent *X*-ray powder pattern was obtained using a Guinier Simon camera FR 553 (Enraf–Nonius).[14]

Theoretical Investigations.—In *ab initio* Hartree–Fock calculations the effective core potential approximation (e.c.p.)

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† Dipotassium bis(2,2-dicyanoethylene-1,1-dithiolato)plumbate(II) dihydrate.

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

for the core electrons of Pb was used. The e.c.p. parameters were obtained from atomic relativistic Hartree–Fock calculations.[15] A minimal basis set was taken for the valence electrons of Pb[15] and a Clementis well balanced basis set was employed for the ligand atoms S, C, and O (for sulphur 9*s*/5*p* contracted to 3*s*/2*p* and 7*s*/3*p* contracted to 2*s*/1*p* for carbon and oxygen).[16,*] This minimal basis set has been shown to be of almost double-zeta quality.

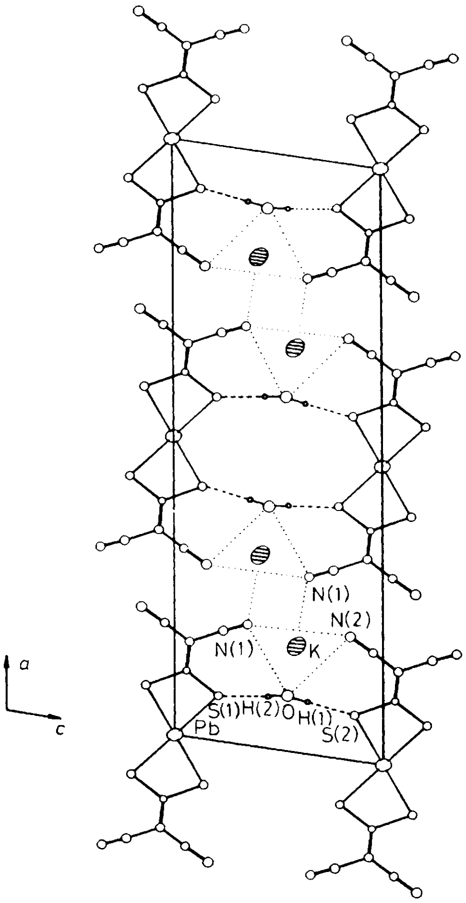

Figure 1. Unit cell of $K_2[Pb\{S_2C=C(CN)_2\}_2]\cdot 2H_2O$ as a projection on the *ac* plane

Ab initio Hartree–Fock crystal orbital calculations for the energy band structure of poly($[Pb\{S_2C=C(CN)_2\}_2]^{2-}$ 2+) were also performed using the above described basis sets. The positive counter ions were replaced by two point charges at the corresponding positions in the crystal structure. All calculations were carried out on a CYBER 845 at Regionales Rechenzentrum der Universität Erlangen–Nürnberg.

Results and Discussion

Crystal Structure.—The atomic co-ordinates are listed in Table 1. A projection of the structure on the *ac* plane is depicted in Figure 1. Pyramidal $[Pb\{S_2C=C(CN)_2\}_2]^{2-}$ anions are stacked along the crystallographic *b* axis. In the cavities of the columns are the potassium ions in a monocapped trigonal-pyramidal arrangement. The water molecules are co-ordinated to potassium and are involved in two S • • • H hydrogen bonds (monofurcated).[19,20] Table 2 contains characteristic bond lengths and angles, while Figure 2 shows the pyramidal $[Pb\{S_2C=C(CN)_2\}_2]^{2-}$ anion.

The overall symmetry of the complex anion is C_2 with an apparently stereochemically active lone pair located on the two-fold axis. The ligand acts as a symmetric chelating agent with Pb–S 2.88 Å. This value is in the middle of the range usually observed: 2.58 Å for single bonds and 3.04 Å for ionic Pb • • • S contacts.[21,22] The value of 1.28 Å for the C(1)–C(2) distance corresponds to a strong localized double bond,[23] while other interatomic distances in the ligand are as commonly observed.[24,25]

Thermal Investigations.—On continuous heating the compound loses crystal water at about 65 °C. The water-poor

Table 1. Final fractional co-ordinates for $K_2[Pb\{S_2C=C(CN)_2\}_2]\cdot 2H_2O$ with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*
Pb	0.0	0.0	0.0
K	0.178 1(5)	0.299(3)	0.586(1)
S(1)	0.076 8(5)	0.387(3)	0.211(1)
S(2)	0.076 4(5)	0.388(3)	0.861(1)
C(1)	0.610(1)	0.046(12)	0.057(4)
C(2)	0.659(2)	0.147(10)	0.071(5)
C(3)	0.315(2)	0.231(11)	0.766(5)
C(4)	0.686(2)	0.242(10)	0.955(5)
N(1)	0.703(2)	0.304(9)	0.351(5)
N(2)	0.707(2)	0.308(10)	0.842(5)
O	0.405(2)	0.342(9)	0.454(5)
H(1)	0.414(9)	0.480(16)	0.367(10)
H(2)	0.418(10)	0.464(16)	0.552(7)

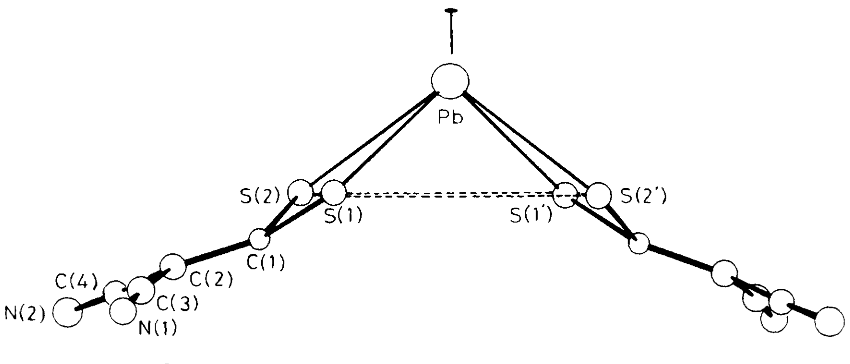

Figure 2. View of the $[Pb\{S_2C=C(CN)_2\}_2]^{2-}$ anion showing the pyramidal geometry with overall symmetry C_2

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[*] During all calculations the isolobal dithiocarbonate anion was used instead of $[S_2C=C(CN)_2]^{2-}$. As a justification of this it could be shown that there was no significant influence on the results using this element displacement formalism.[17,18]

Table 2. Bond lengths (Å) and angles (°) for $K_2[Pb\{S_2C=C(CN)_2\}_2]\cdot 2H_2O$

(*a*) The potassium ion					
K–O	2.77(4)	3.02(4)			
K–N(1)	2.95(3)	2.97(4)	3.00(4)		
K–N(2)	2.95(5)	3.01(5)			
(*b*) The lead ion					
Pb–S(1)	2.88(1)			S(1)–Pb–S(1′)	113.6(3)
Pb–S(2)	2.88(1)			S(2)–Pb–S(2′)	113.3(3)
				S(1)–Pb–S(2)	62.0(3)
				S(1)–Pb–S(2′)	82.4(3)
Elevation over S_4 plane: 1.58(1)					
(*c*) The ligand					
S(1)–S(2)	2.97(2)	(bite)			
S(1)–S(2′)	3.79(2)			S(1)–C(1)–S(2)	110(2)
C(1)–S(1)	1.78(4)			C(2)–C(1)–S(1)	127(3)
C(1)–S(2)	1.85(4)			C(2)–C(1)–S(2)	119(3)
C(1)–C(2)	1.28(5)			C(3)–C(2)–C(4)	115(4)
C(2)–C(3)	1.47(6)			C(1)–C(2)–C(3)	117(4)
C(2)–C(4)	1.34(6)			C(1)–C(2)–C(4)	128(4)
C(3)–N(1)	1.06(6)			C(2)–C(3)–N(1)	176(5)
C(4)–N(2)	1.19(6)			C(2)–C(4)–N(2)	175(5)
(*d*) The hydrogen bonds					
S(1)···H(2)	2.63(6)			H(1)–O–H(2)	105(9)
S(2)···H(1)	2.59(9)				
S(1)···O	3.37(4)				
S(2)···O	3.34(4)				

Least-squares plane: $0.473x - 0.878y + 0.073z = 0$. Deviations (Å): S(1), 0.0; S(2), 0.0; C(1), −0.176; C(2), 0.046; C(3), 0.059; C(4), 0.030; N(1), −0.003; N(2), 0.044.

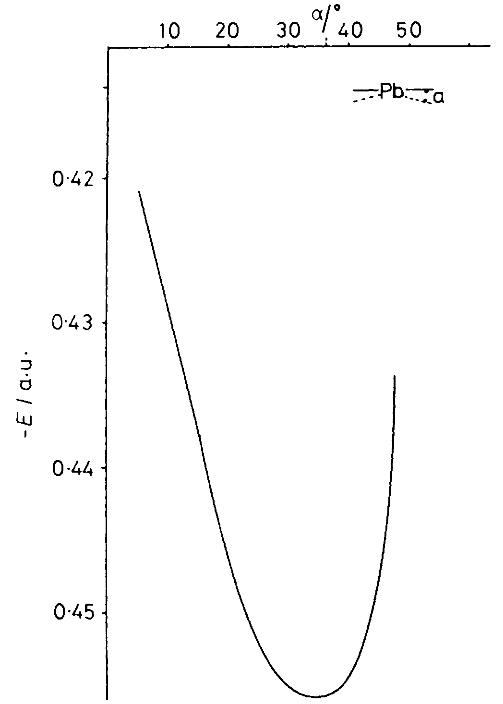

Figure 3. Results of energy calculations for different geometries of the anion $[Pb(S_2CO)_2]^{2-}$ · 1 a.u. = 2.6264×10^6J

product is stable up to 120 °C. A second phase transition occurs at 200 °C. The corresponding powder diffraction pattern indicates a transition from low to high symmetry. Further investigations are necessary to decide whether this effect corresponds to a transition involving pyro- and para-electrical phases. Decomposition of the substance occurs at about 220 °C. For $T > 220$ °C only the powder pattern of PbS is detectable while the rest of the heterogeneous mixture seems to be *X*-ray amorphous.[26] At a temperature of 311 °C, CS_2 is squeezed out and can easily be identified by mass spectroscopy and the corresponding mass decrease in the t.g. curve. A small increase of the sample mass at 442 °C is due to oxidation caused by oxygen contamination of the nitrogen atmosphere used in the experiment.

Calculations.—The aims of the calculations in the present study are two-fold. First it was intended to estimate the relative stability of one pyramidal $[Pb\{S_2C=C(CN)_2\}_2]^{2-}$ group as a function of the bending angle α (Figure 3) to elucidate the influence of packing effects on the molecule geometry of one repeat unit of the polymer. Secondly, to understand the solid state electronic environment of this polymer, we have performed *ab initio* Hartree–Fock crystal orbital calculations for the energy band structure using the observed geometry. During all calculations the e.c.p. formalism for the lead atom combined with minimal basis sets for the valence electrons of Pb, S, C, and O was used. Figure 4 correlates total energies for anions $[Pb(S_2CO)_2]^{2-}$ with the deviation from planar geometry on changing the bending angle α. The minimum of the resulting curve is at α = 38°. A value for α of 39.8° results from the *X*-ray structure of $[Pb\{S_2C=C(CN)_2\}_2]^{2-}$. This is obviously due to small influences of packing effects on single pyramidal $Pb\{S_2C=C(CN)_2\}_2$ units and justifies the use of dithiocarbonate instead of the present ligand. The stabilization of the pyramidal arrangement is predominantly due to a straightforward mixing of the 6*s* orbital of Pb with *p*-type orbitals located on the ligands in going from a planar to a pyramidal geometry.

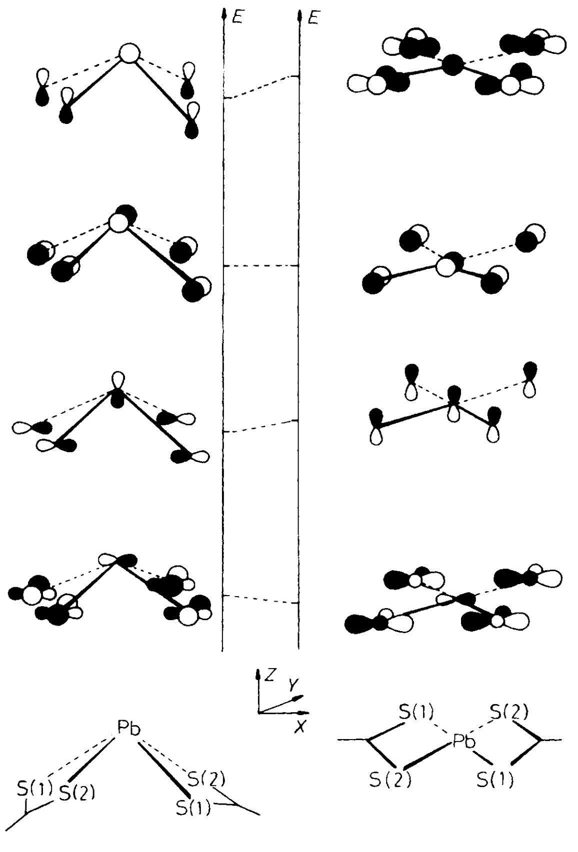

Figure 4. Correlation of the four highest occupied molecular orbitals of $[Pb(S_2CO)_2]^{2-}$ in the planar and pyramidal arrangements

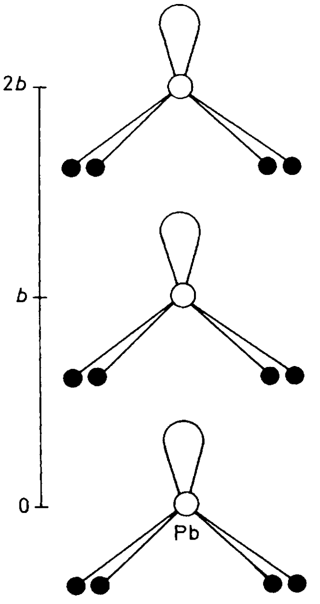

Figure 5. Within one chain of poly-$[Pb\{S_2C{=}C(CN)_2\}_2]^{2-}$ all lone pairs show the same direction without attractive interactions between them

The stabilization energy between the two extreme geometries is 25 kcal mol^{-1} (104.6 kJ mol^{-1}). A population analysis[27] for $[Pb(S_2CO)_2]^{2-}$ shows the donating character of the 1,1-dithiolate because Pb has a net charge of +0.56 instead of +2 (total number of electrons for the ligand: S, 16.39; C, 6.03; O, 8.47).

In order to shed some light on the intramolecular interaction within the linear chain of anions we have performed *ab initio* Hartree–Fock crystal orbital calculations for the energy band of the polymer as described above. It has recently been shown that results for band structures obtained with the use of mixed basis sets, valence electron basis for some of the atoms and all-electron basis for the others, are in very good agreement with results obtained when employing all-electron basis sets for all atoms.[28] Comparing the total energy per elementary cell with the energy of an isolated unit, one finds that the linear chain is not stabilized. This is not surprising because the simple translational periodicity leads to unfavourable relative orientations of the polymer units with respect to dipole–dipole interactions, although it is sometimes stated that Pb • • • Pb distances of about 4 Å are indicative of weak bonding interactions.[29]

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