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The Complexing Properties of 1-Aminosquarate Derivatives with Lead

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Reaction of three different 1-(dialkylamino) derivatives of 3,4-dihydroxycyclobut-3-ene-1,2-dione (squaric acid) with lead(II) nitrate in aqueous solution yielded polymeric complexes which have been characterized by single-crystal X-ray analysis. $Pb[(CH_3)_2NC_4O_3]_2(OH_2)_2\cdot H_2O$ (**1**) produced from 1-(dimethylamino)-2-methoxycyclobutenedione crystallizes in the triclinic space group $P\bar{1}$, with $a = 8.591(5)$ Å, $b = 9.308(4)$ Å, $c = 10.571(4)$ Å, $\alpha = 95.58(2)°$, $\beta = 94.96(3)°$, $\gamma = 95.78(4)°$, and $Z = 2$. The complex of formula $Pb[(C_2H_5)_2NC_4O_3]_2(H_2O)$ (**2**) formed from the corresponding 1-(diethylamino) analogue of the ligand also crystallizes in space group $P\bar{1}$, with $a = 7.521(2)$ Å, $b = 10.928(4)$ Å, $c = 11.749(4)$ Å, $\alpha = 90.10(2)°$, $\beta = 97.84(2)°$, $\gamma = 95.12(2)°$, and $Z = 2$. In both of these complexes, the lead atom is eight-coordinate with the ligands being bound in bidentate and binucleating fashions. The di-*n*-propylamino substituent in the di-*n*-propyl homologue hydrolyzed during crystallization, and a lead(II) squarate, $Pb(C_4O_4)(H_2O)_4$ (**3**), was produced: monoclinic space group $P2_1$, with $a = 6.466(2)$ Å, $b = 7.898(3)$ Å, $c = 8.307(3)$ Å, $\beta = 92.88(3)°$, and $Z = 2$. The lead atom is again eight-coordinate, and the squarate moiety, bidentate and binucleating. The respective coordination polyhedra for the complexes are square antiprismatic (**1**), bicapped trigonal prismatic (**2**), and distorted mono faced-capped and edge-capped trigonal prismatic (**3**).

Introduction

The complexing properties of squaric acid have been extensively investigated since its initial synthesis in 1959.[1] These investigations have revealed a variety of coordination modes: monodentate, bidentate, bridging—both cis-1,2- and μ-1,3-bismonodentate—and in some instances a co-existence of these modes in the same complex. Comparable investigations into the complexing properties of substituted squarate ligands, however, have not been carried out. Here we report on the effects on the complexing properties of this ligand when amino substituents of increasing R size (R = alkyl) are substituted on the ring. In particular, we hoped to gain information as to how (a) the coordination polyhedron about the central metal atom, (b) the coordination mode(s) of the ligand(s), and (c) the extent and nature of any H-bonding might be affected, individually or collectively, by R size. We have already shown that these factors can be important in determining the form of the polymer structure and the nature of the supramolecular H-bonded array observed in lead(II) aminosquarate.[2] It is envisaged that these Pb complexes might act as prototypes for the synthesis of analogous complexes of lanthanides, which have similar ionic radii and/or coordination number. This would then permit investigation into phenomena, such as antiferromagnetic coupling, molecular magnetism, and others based on linearly arranged and/or bridged metal atoms which can communicate with each other.[1d,g,3]

Experimental Section

Preparation of Ligands. The 1-(dimethylamino)-2-methoxycyclobutenedione was obtained by bubbling gaseous dimethylamine (99%) obtained from Aldrich through an ethereal solution of dimethyl squarate (prepared according to the method of Cohen and Cohen).[4] The mixture was then evaporated to dryness on a rotary evaporator and the crude product recrystallized from methanol. ^{1}H NMR (200 MHz, DMSO-d_6): δ 3.00 (s, 3H), 3.17 (s, 3H), 3.35 (s, 3H).

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Table 1. Crystallographic Data for $Pb[(CH_3)_2NC_4O_3]_2(OH_2)_2 \cdot H_2O$ (**1**), $Pb[(C_2H_5)_2NC_4O_3]_2(H_2O)$ (**2**), and $Pb(C_4O_4)(H_2O)_4$ (**3**)

	1	2	3
formula	$C_{12}H_{18}N_2O_9Pb$	$C_{16}H_{22}N_2O_7Pb$	$C_4H_8O_8Pb$
fw	541.5	561.5	391.3
space group	$P\bar{1}$	$P\bar{1}$	$P2_1$
a, Å	8.591(5)	7.521(2)	6.466(2)
b, Å	9.308(4)	10.928(4)	7.898(3)
c, Å	10.571(4)	11.749(4)	8.307(3)
α, deg	95.58(2)	90.10(2)	
β, deg	94.96(3)	97.84(2)	92.88(3)
γ, deg	95.78(4)	95.12(2)	
V, Å^3	833.1(6)	952.7(5)	423.7(3)
Z	2	2	2
ρ_{calc}, g cm^{-3}	2.158	1.957	3.067
λ, Å	0.710 73	1.541 78	0.710 73
μ, mm^{-1}	10.174	17.576	19.925
T, °C	−50	20	20
R^a	0.0622	0.0327	0.0266
$R_w{}^b$	0.1505^c	0.0347	0.0678^c

[a] $R = \sum|F_o - F_c|/\sum|F_o|$. [b] $R_w = \sum[|F_o - F_c|w^{1/2}]/\sum[|F_o|w^{1/2}]$. $w^{-1} = [\sigma^2(F_o) + g(F_o{}^2)]$. [c] wR_2 (SHELXL-93).

1-(Diethylamino)-2-methoxycyclobutenedione. This was prepared by adding redistilled diethylamine dropwise from a syringe to an ethereal solution of dimethyl squarate until no further precipitation was observed. The mixture was then evaporated to dryness on a rotary evaporator and the crude product recrystallized from ethanol. ^1H NMR (270 MHz, $CDCl_3$): δ 1.24 (m, 6H), 3.45 (q, $J = 7.2$ Hz, 2H), 3.73 (q, $J = 7.2$ Hz, 2H), 4.44 (s, 3H).

1-(Di-*n*-propylamino)-2-methoxycyclobutenedione. This was prepared similarly to the diethylamino analogue except that the mixture of the di-*n*-propylamine and the ethereal solution of dimethyl squarate was refluxed for 2 h under anhydrous conditions. The product was recrystallized from ethanol. ^1H NMR (270 MHz, $CDCl_3$): δ 0.95 (m, 6H), 1.65 (m, 4H), 3.34 (t, $J = 7.2$ Hz, 2H), 3.64 (t, $J = 7.2$ Hz, 2H), 4.40 (s, 3H).

Preparation of the Lead Complexes. Aqueous solutions of the ligands were mixed with equimolar solutions of AR grade $Pb(NO_3)_2$. Any initial formation of precipitate was removed by filtration and the filtrate left to evaporate slowly until crystal formation was complete. The methoxy derivatives of the 1-(dialkylamino)squarate ligands were used in these syntheses in order to achieve conditions similar to those used in the preparation of lead(II) aminosquarate[2] since a comparative study was intended.

$Pb[(CH_3)_2NC_4O_3]_2(OH_2)_2 \cdot H_2O$: Clear, colorless platy needles (40% yield). Anal. Calc for $C_{12}H_{18}N_2O_9Pb$: C, 26.62; H, 3.33; N, 4.37; Pb, 38.26. Found: C, 26.88; H, 3.80; N, 5.13; Pb, 38.70.

$Pb[(C_2H_5)_2NC_4O_3]_2(H_2O)$: Clear, colorless platy needles (35% yield). Anal. Calc for $C_{16}H_{22}N_2O_7Pb$: C, 34.22; H, 3.92; N, 4.99; Pb, 36.90. Found: C, 34.60; H, 4.00; N, 5.20; Pb, 37.10.

$Pb(C_4O_4)(H_2O)_4$: Colorless needles (38% yield). Anal. Calc for $C_4H_8O_8Pb$: C, 12.28; H, 2.05, Pb, 52.94. Found: C, 12.86; H, 2.70; Pb, 53.00.

Elemental Analyses. C, H, N analyses were done by MEDAC Limited, Brunel University, Uxbridge, Middlesex, U.K. The Pb analyses were done by flame atomic absorption spectrophotometry using a Unicam 929 atomic absorption spectrometer.

NMR Spectra. The NMR spectra were done on a JEOL EX270 and a Varian Gemini 200.

Table 2. Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters[a] (Å^2 × 10^3) for **1**

	x	y	z	U(eq)
Pb	−2503(1)	−163(1)	190(1)	23(1)
O(1)	−5167(11)	−1720(10)	−147(9)	27(2)
C(2)	−5757(16)	−2690(13)	459(12)	21(3)
C(3)	−7343(15)	−3127(14)	722(13)	24(3)
C(4)	−6780(17)	−4239(15)	1469(13)	27(3)
C(5)	−5172(16)	−3819(15)	1193(13)	26(3)
O(6)	−8642(11)	−2674(11)	407(10)	35(2)
N(7)	−7454(14)	−5205(13)	2125(11)	29(3)
C(8)	−9142(20)	−5331(19)	2252(18)	46(4)
C(9)	−6565(20)	−6255(16)	2719(16)	40(4)
O(10)	−3880(12)	−4237(11)	1513(11)	37(2)
O(11)	145(11)	464(11)	1557(9)	28(2)
C(12)	699(15)	−175(14)	2468(12)	22(3)
C(13)	109(16)	−893(15)	3514(12)	26(3)
C(14)	1706(16)	−1216(14)	3890(12)	24(3)
C(15)	2288(16)	−450(15)	2877(11)	24(3)
O(16)	−1192(12)	−1181(12)	3924(10)	35(2)
N(17)	2335(15)	−1985(13)	4727(12)	32(3)
C(18)	1398(20)	−2664(18)	5641(14)	39(4)
C(19)	4000(17)	−2177(18)	4833(15)	36(3)
O(20)	3587(11)	−141(12)	2438(9)	31(2)
O(21)	−3290(12)	−154(13)	2349(10)	37(3)
O(22)	−1730(12)	−2589(12)	481(13)	45(3)
O(30)	−2629(18)	−4021(15)	4113(13)	60(3)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Table 3. Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Coefficients[a] (Å^2 × 10^3) for **2**

	x	y	z	U(eq)
Pb	2206(1)	4638(1)	4012(1)	36(1)
O(1)	−367(6)	3700(4)	5287(4)	47(1)
C(1)	249(8)	2772(5)	5784(5)	44(2)
O(2)	3238(6)	2504(4)	5236(4)	55(2)
C(2)	1906(8)	2234(6)	5720(6)	47(2)
C(3)	1362(10)	1272(7)	6524(7)	58(2)
N(3)	2067(10)	326(6)	6999(7)	76(3)
C(4)	−355(9)	1809(6)	6548(7)	54(2)
O(4)	−1690(8)	1561(5)	7038(6)	80(2)
C(5)	3877(15)	6(10)	6802(11)	105(5)
C(6)	3902(25)	−967(12)	6148(19)	200(13)
C(7)	1077(13)	−457(8)	7757(9)	83(4)
C(8)	−175(16)	−1309(10)	7110(10)	101(4)
O(11)	6024(6)	4621(4)	4129(3)	45(1)
C(11)	6244(8)	4345(5)	3137(5)	41(2)
O(12)	3255(6)	3635(5)	2063(4)	58(2)
C(12)	4915(9)	3871(6)	2172(5)	44(2)
C(13)	6354(7)	3891(5)	1435(5)	39(2)
N(13)	6400(8)	3639(6)	355(4)	56(2)
C(14)	7678(8)	4370(6)	2389(5)	42(2)
O(14)	9330(6)	4703(5)	2483(4)	61(2)
C(15)	4732(11)	3158(8)	−367(6)	67(3)
C(16)	4288(17)	1808(10)	−237(11)	115(5)
C(17)	8046(11)	3897(9)	−162(7)	70(3)
C(18)	9081(17)	2868(16)	−335(13)	134(7)
O(20)	3740(6)	6551(4)	3268(4)	52(1)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Crystallographic Analyses. Crystal data for **1**−**3** and a summary of the crystallographic analyses are given in Table 1. The data were collected on a Siemens P4/PC diffractometer using graphite-monochromated Mo Kα radiation for **1** and **3** and on a Siemens P4/RA diffractometer using graphite-monochromated Cu Kα radiation for **2**. ω-scans were used for all three data collections, and the data were corrected for Lorentz and polarization factors and for absorption. Structures **1** and **2** were solved by direct methods, and **3** was solved by the heavy atom method. In all three structures, all the non-hydrogen atoms were refined anisotropically. For structures **1** and **3**, hydrogen atoms were not located; in **1** the methyl hydrogens were placed in calculated positions and assigned isotropic thermal parameters, $U(H) = 1.5U_{eq}(C)$. In structure **2**, all the hydrogen atoms were located from a ΔF map; the C−H hydrogens were optimized and assigned isotropic thermal parameters, $U(H) = 1.2U_{eq}(C)$. The aqua hydrogens were refined isotropically subject to an O−H distance constraint, O−H 0.90 Å. Refinements were by full-matrix least squares; those for **1** and **3** were based on F^2, and those for **2**, on F. Computations were carried out on 486 and pentium PCs using the SHELXL system, versions 4.2 and 5.03.[5] Fractional atomic coordinates and equivalent isotropic thermal parameters for compounds **1**−**3** are given in Tables 2−4, respectively, and selected bond lengths and angles, in Tables 5−7.

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(5) Sheldrick, G. M. SHELXL versions 4.2 and 5.03, Siemens Analytical X-ray Instruments Inc., Madison, WI, 1990 and 1994.

Table 4. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters[a] ($Å^2 \times 10^3$) for **3**

	x	*y*	*z*	*U*(eq)
Pb	267(1)	763(7)	1213(1)	24(1)
O(1)	972(37)	2793(22)	−1380(26)	30(5)
C(2)	1450(39)	1774(31)	−2529(26)	10(4)
C(3)	2220(32)	1773(29)	−4118(27)	17(4)
O(3)	2521(53)	2913(30)	−5152(37)	39(6)
C(4)	1817(33)	−85(36)	−4241(30)	22(5)
O(4)	2299(48)	−1144(31)	−5179(34)	32(5)
C(5)	1285(60)	−22(48)	−2447(45)	36(8)
O(6)	1068(37)	−1073(26)	−1377(19)	29(5)
O(7)	−2322(15)	874(40)	3539(9)	37(3)
O(8)	−3125(12)	874(38)	−235(8)	30(2)
O(9)	3933(30)	−1447(23)	1944(26)	21(3)
O(10)	4130(39)	2751(24)	1842(31)	38(5)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Table 5. Selected Bond Lengths (Å) and Angles (deg) for **1**[a]

Pb−O(21)	2.435(10)	Pb−O(22)	2.456(10)
Pb−O(1)	2.560(10)	Pb−O(11)	2.569(9)
Pb−O(1)#1	2.791(9)	Pb−O(6)#1	2.873(10)
Pb−O(11)#2	2.873(10)	Pb−O(20)#2	2.903(10)
O(1)−Pb#1	2.791(9)	O(11)−Pb#2	2.873(10)
O(6)−Pb#1	2.873(10)	O(20)−Pb#2	2.903(10)
O(21)−Pb−O(22)	85.5(4)	O(21)−Pb−O(1)	77.2(3)
O(22)−Pb−O(1)	78.4(3)	O(21)−Pb−O(11)	78.0(3)
O(22)−Pb−O(11)	78.4(4)	O(1)−Pb−O(11)	147.1(3)
O(21)−Pb−O(1)#1	78.2(3)	O(22)−Pb−O(1)#1	149.1(3)
O(1)−Pb−O(1)#1	72.4(3)	O(11)−Pb−O(1)#1	122.6(3)
O(21)−Pb−O(6)#1	112.9(4)	O(22)−Pb−O(6)#1	143.4(3)
O(1)−Pb−O(6)#1	134.9(3)	O(11)−Pb−O(6)#1	75.3(3)
O(1)#1−Pb−O(6)#1	67.5(3)	O(21)−Pb−O(11)#2	149.9(3)
O(22)−Pb−O(11)#2	77.4(3)	O(1)−Pb−O(11)#2	122.2(3)
O(11)−Pb−O(11)#2	74.5(3)	O(1)#1−Pb−O(11)#2	127.4(3)
O(6)#1−Pb−O(11)#2	71.4(3)	O(21)−Pb−O(20)#2	144.1(3)
O(22)−Pb−O(20)#2	112.9(4)	O(1)−Pb−O(20)#2	76.9(3)
O(11)−Pb−O(20)#2	134.2(3)	O(1)#1−Pb−O(20)#2	70.5(3)
O(6)#1−Pb−O(20)#2	70.9(3)	O(11)#2−Pb−O(20)#2	66.0(3)

[a] Symmetry transformations used to generate equivalent atoms: (#1) $-x-1, -y, -z$; (#2) $-x, -y, -z$.

Table 6. Selected Bond Lengths (Å) and Angles (deg) for **2**

Pb−O(1)	2.736(4)	Pb−O(2)	2.853(5)
Pb−O(11)	2.858(4)	Pb−O(12)	2.775(5)
Pb−O(20)	2.514(5)	Pb−O(1A)	2.578(4)
Pb−O(11A)	2.491(4)	Pb−O(14A)	2.622(4)
O(14)−PbA	2.622(4)	O(1)−PbB	2.578(4)
		O(11)−PbC	2.491(4)
O(1)−Pb−O(2)	67.9(1)	O(1)−Pb−O(11)	136.0(1)
O(2)−Pb−O(11)	72.2(1)	O(1)−Pb−O(12)	128.4(1)
O(2)−Pb−O(12)	88.6(2)	O(11)−Pb−O(12)	66.7(1)
O(1)−Pb−O(20)	145.9(1)	O(2)−Pb−O(20)	137.5(1)
O(11)−Pb−O(20)	65.8(1)	O(12)−Pb−O(20)	81.4(2)
O(1)−Pb−O(1A)	67.2(1)	O(2)−Pb−O(1A)	126.3(1)
O(11)−Pb−O(1A)	129.2(1)	O(12)−Pb−O(1A)	143.4(1)
O(20)−Pb−O(1A)	78.8(1)	O(1)−Pb−O(11A)	86.3(1)
O(2)−Pb−O(11A)	73.5(1)	O(11)−Pb−O(11A)	64.9(2)
O(12)−Pb−O(11A)	131.5(1)	O(20)−Pb−O(11A)	82.7(1)
O(1A)−Pb−O(11A)	75.9(1)	O(1)−Pb−O−(14A)	80.4(1)
O(2)−Pb−O(14A)	124.9(2)	O(11)−Pb−O(14A)	140.0(1)
O(12)−Pb−O(14A)	77.1(1)	O(20)−Pb−O(14A)	93.0(2)
O(1A)−Pb−O(14A)	73.6(1)	O(11A)−Pb−O(14A)	149.4(2)

Table 7. Selected Bond Lengths (Å) and Angles (deg) for **3**[a]

Pb−O(8)	2.450(7)	Pb−O(1)#1	2.48(2)
Pb−O(7)	2.621(7)	Pb−O(6)#2	2.65(2)
Pb−O(6)	2.67(2)	Pb−O(1)	2.74(2)
Pb−O(10)	2.97(3)	Pb−O(9)	2.98(2)
O(1)−Pb#2	2.48(2)	O(6)−Pb#1	2.65(2)
O(8)−Pb−O(1)#1	77.2(9)	O(8)−Pb−O(7)	76.8(3)
O(1)#1−Pb−O(7)	76.7(9)	O(8)−Pb−O(6)#2	72.9(9)
O(1)#1−Pb−O(6)#2	141.3(3)	O(7)−Pb−O(6)#2	73.1(8)
O(8)−Pb−O(6)	80.1(7)	O(1)#1−Pb−O(6)	66.9(6)
O(7)−Pb−O(6)	140.4(8)	O(6)#2−Pb−O(6)	129.2(5)
O(8)−Pb−O(1)	76.9(7)	O(1)#1−Pb−O(1)	131.5(4)
O(7)−Pb−O(1)	134.2(7)	O(6)#2−Pb−O(1)	63.7(5)
O(6)−Pb−O(1)	68.7(3)	O(8)−Pb−O(10)	142.3(8)
O(1)#1−Pb−O(10)	139.4(7)	O(7)−Pb−O(10)	114.5(7)
O(6)#2−Pb−O(10)	76.5(6)	O(6)−Pb−O(10)	103.5(7)
O(1)−Pb−O(10)	70.0(7)	O(8)−Pb−O(9)	143.5(7)
O(1)#1−Pb−O(9)	72.0(6)	O(7)−Pb−O(9)	113.6(5)
O(6)#2−Pb−O(9)	143.1(6)	O(6)−Pb−O(9)	70.2(6)
O(1)−Pb−O(9)	109.9(6)	O(10)−Pb−O(9)	67.7(4)

[a] Symmetry transformations used to generate equivalent atoms: (#1) $-x, y-{}^{1}/_{2}, -z$; (#2) $-x, y+{}^{1}/_{2}, -z$.

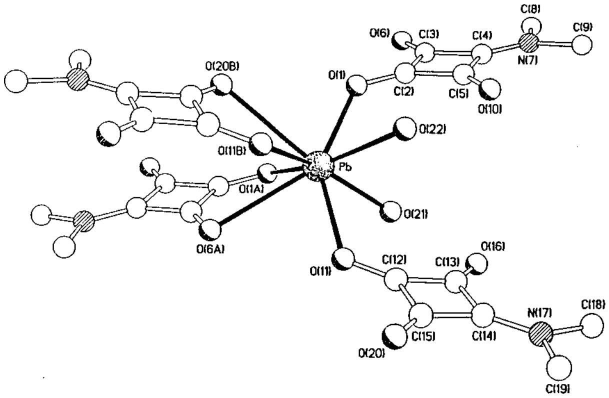

Figure 1. Environment of the Pb atoms in the structure of **1**.

Results and Discussion

After the synthesis and structural elucidation of lead(II) aminosquarate, it was decided to synthesize a series of lead(II) complexes using the higher aminosquarate homologues where R = CH_3, C_2H_5, and *n*-C_3H_7. As mentioned before (vide supra), the major objective of this study was to investigate the effect of increasing the size of the R group on the complexing properties of the ligand with lead. In complexes **1** and **2**, the respective amino groups were retained by the ligand during complexation. However, there is no evidence for the presence of the amino group in complex **3**. Elemental analysis of **3** showed no nitrogen, and the X-ray structure did not reveal the existence of any *n*-propyl groups. The NMR spectrum of the ligand 1-(di-*n*-propylamino)-2-methoxycyclobutenedione used in the preparation of **3** clearly identified the protons on the *n*-propyl groups. It is clear then that the di-*n*-propylamino group was hydrolyzed during the crystallization process. The hydrolysis of the methoxy group also occurred during the formation of each complex since the X-ray structure in each case showed no OCH_3 groups attached to the ligand C4 rings. Hydrolysis of methoxy derivatives of squaric acid in water has been shown to occur.[4] A similar change was observed in the preparation of lead(II) aminosquarate.[2]

Structure of $Pb[(CH_3)_2NC_4O_3]_2(OH_2)_2{\cdot}H_2O$ (1). The X-ray analysis of **1** shows the complex to be polymeric with the constitution $\{Pb[(CH_3)_2NC_4O_3]_2(H_2O)_2{\cdot}H_2O\}_n$. Each (dimethylamino)squarate ligand is bidentate with two of the three O atoms being coordinated to the Pb center (Figure 1). The third O atom in each independent ligand O(10) and O(16) is involved only in H-bonding, to the included H_2O molecule [2.84 Å, O(10); 2.84 Å, O(16)] and to one each of the coordinated aqua ligands of an adjacent Pb center [2.66 Å, O(10)···O(22); 2.66 Å, O(16)···O(21)]. One of the two coordinated O atoms of each ligand, O(1) and O(11), has a dual role, being binucleating and serving to link adjacent Pb atoms in the polymer chain. Each Pb center is eight-coordinate being bound to six ligand O

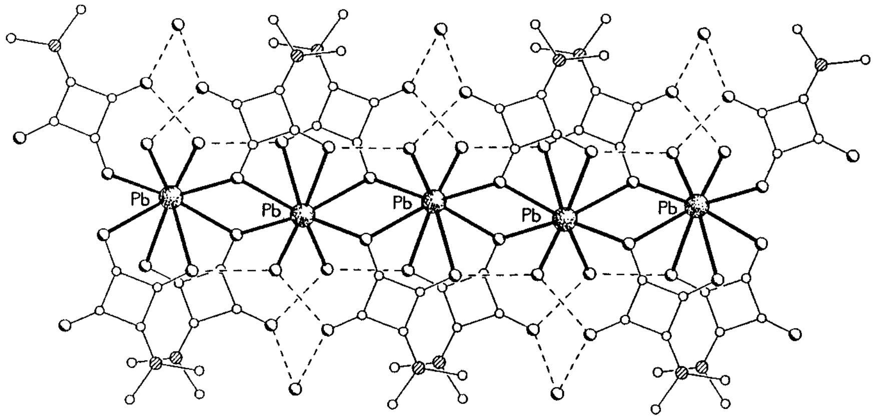

Figure 2. Part of one of the O-bridged and H-bonded polymeric ribbons in the structure of **1**.

atoms and two aqua ligands in a slightly distorted square antiprismatic geometry.

The Pb−O (ligand) distances are in the range 2.56(1)−2.90(1) Å, the two Pb−O(aqua) distances being noticeably shorter at 2.44(1) and 2.46(1) Å. Each crystallographically independent centrosymmetric Pb_2O_2 ring is planar with asymmetric Pb−O−Pb bridges [2.56(1) and 2.79(1) Å for O(1) and 2.57(1) and 2.87(1) Å for O(11)] (Figure 2). Each of these rings is inclined ~76° to the next one in the chain; the associated nonbonded, transannular Pb···Pb distances are 4.32(1) and 4.34(1) Å, respectively. The vectors linking adjacent Pb atoms within the polymer chains form a zigzag with adjacent Pb···Pb vectors subtending an angle of 166°.

The oxygen bridging of the metal centers together with additional H-bonding interactions involving both the coordinated and included H_2O molecules combine to form a flattened ribbonlike polymer whose chains extend in the crystallographic *a* direction. The outer edges of the ribbons are populated by the dimethylamino groups and the noncoordinated included water molecules. There is an absence of any significant interribbon interactions other than van der Waals.

Structure of $Pb[(C_2H_5)_2NC_4O_3]_2(H_2O)$ (2). Complex **2** is also polymeric and is found to have the formulation $\{Pb[(C_2H_5)_2NC_4O_3]_2(H_2O)\}_n$. There are thus, as in **1**, two independent ligands for each Pb atom (Figure 3). However, their mode of binding within the polymeric structure is different. One of the ligands is bidentate coordinating to the Pb center via O(1) and O(2), O(1) also having a binucleating role bridging to a centrosymmetrically related Pb center forming a planar Pb_2O_2 ring. The third O atom in this ligand, O(4), does not have a coordinating role but is involved in intrachain H-bonding (2.68 Å) to the aqua ligand O(20) on an adjacent Pb center. The coordinated ligand oxygen O(2) is also involved in a similar intrachain H-bonding interaction (2.79 Å) with an adjacent coordinated aqua ligand. The other independent aminosquarate ligand is also bidentate, binding to the metal center via O(11) and O(12), and with O(11) also having a binucleating role, forming a link to another Pb atom across a different crystallographic symmetry center creating a second planar Pb_2O_2 ring. The third O atom O(14) is coordinated to an adjacent Pb center, the ligand thus forming a secondary 1,2-cis bridge.

As in **1**, the Pb atom is eight-coordinate but in this instance has a bicapped trigonal prismatic geometry. The Pb−O distances are in the range 2.514(5) Å for the coordinated aqua ligand to 2.858(4) Å for O(11). Both of the Pb_2O_2 rings have asymmetric Pb−O bridges, 2.578(4) and 2.736(4) Å for O(1) and 2.491(4) and 2.858(4) Å for O(11). The nonbonded transannular Pb···Pb separations are 4.43 and 4.52 Å, slightly longer than those observed for **1**. The planes of adjacent Pb_2O_2 rings within the polymeric core are approximately orthogonal (~81°) with respect to each other, but the zigzag nature of the Pb···Pb···Pb vectors is pronounced with adjacent Pb···Pb vectors subtending an angle of 114°. As in **1**, **2** comprises discrete ribbons that extend in the crystallographic *a* direction, there being no interactions between the interleaved peripheral diethylamino groups other than normal van der Waals (Figure 4).

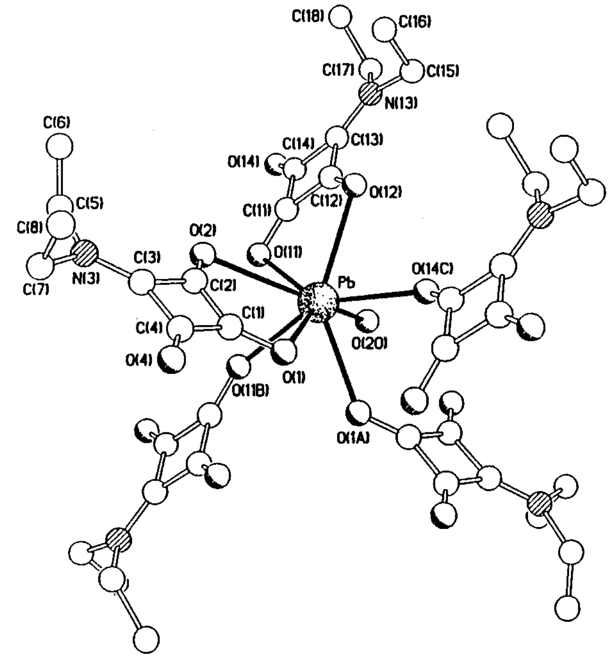

Figure 3. Environment of the Pb atoms in the structure of **2**.

Structure of $Pb(C_4O_4)(H_2O)_4$ (3). The X-ray analysis of **3** reveals a polymeric structure within which the basic repeating unit is $Pb(C_4O_4)(H_2O)_4$. There is only one unique squarate moiety which is bidentate, with the two coordinated O atoms also being binucleating, bridging to adjacent Pb centers and forming a series of linked Pb_2O_2 rings.

The Pb atom is again eight-coordinate with Pb−O distances in the range 2.45(1)−2.98(2) Å. Two of the coordinated waters O(9) and O(10) (depicted by the hatched bonds in Figure 5) are at significantly longer distances (nearly 3 Å) from the Pb center, while the third O(8) has the shortest Pb−O distance. The geometry about the Pb can best be described as mono face-capped and edge-capped trigonal prismatic.

In this complex there is no inversion center within the four-membered Pb_2O_2 rings, and whereas one of the bridges to O(6) is essentially symmetric with Pb−O distances of 2.65(2) and 2.67(2) Å, the other to O(1) is asymmetric with Pb−O distances of 2.48(2) and 2.74(2) Å. Despite the potential freedom for

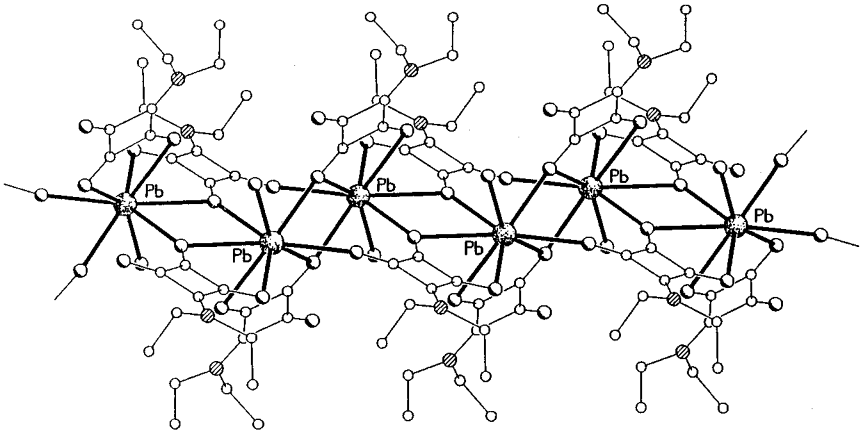

Figure 4. Part of one of the O-bridged and H-bonded polymeric ribbons in the structure of **2**.

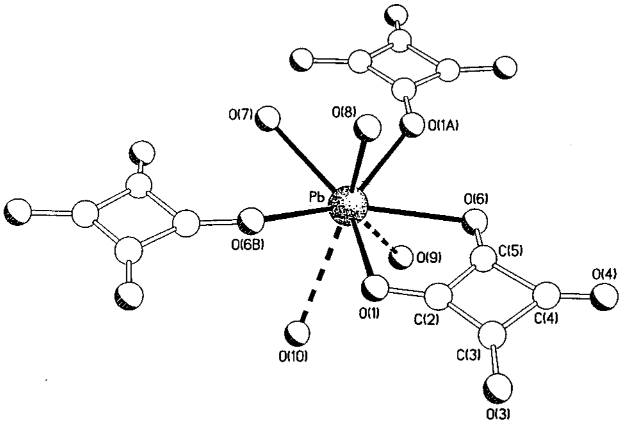

Figure 5. Environment of the Pb atoms in the structure of **3**.

the Pb_2O_2 ring to fold, it is, within statistical significance, planar. Adjacent rings within the polymeric chain, which propagates via the 2_1 screw operator in the crystallographic *b* direction, are oriented with their planes inclined by ~32° to each other. The vectors linking adjacent Pb atoms form a zigzag chain subtending angles of 126° at each Pb center, the nonbonded Pb···Pb separation being 4.44 Å (Figure 6).

Whereas in the structures of **1** and **2**, discrete ribbon polymers are formed and all of the H-bonding interactions are intrachain, here in **3** the coordinated H_2O molecules are involved in both *intra*- and *inter*chain H-bonding interactions with the noncoordinated squarate O atoms; the H-bonded distances are in the range 2.61−2.98 Å. The resultant effect of these interactions is the formation of corrugated sheets that lie in the 100 plane (Figure 7). There is evidence for only weak intersheet H-bonding interactions at ~3.0 Å involving one of the aqua ligands O(8).

Substitution of either an NH_2, NMe_2, or an NEt_2 group on the squarate ring does not change the coordination number of the Pb atom in these squarate complexes.[2] The geometry about the Pb, however, is affected by the nature of the substituent. Complex **1** and lead(II) aminosquarate[2] both exhibit a square antiprismatic geometry about the Pb, while **2** and **3** have trigonal prismatic and mono face-capped, edge-capped trigonal prismatic coordination polyhedra, respectively. It is difficult to say to what extent the size of the amino substituent influences the geometry since the mode of coordination of the ligand and the nature and the extent of hydrogen bonding must also be contributory factors.[6] However, it should be noted that the greatest variation in Pb−O bond lengths (0.53 Å) in these complexes occurs in **3** (Tables 5−7). With the exception of lead(II) aminosquarate,[2] which, unlike the other complexes, has a far more extensive network of H-bonds and a significantly different ligand coordination mode and bridging arrangement, the variation in Pb−O bond lengths decreases with increasing size of the substituent.

In spite of the wide variety of coordination modes shown by squaric acid, it frequently bridges in a μ-1,3- or a tetrakismonodentate manner. For example, in nickel squarate dihydrate,[1d] the ligand adopts a tetrakismonodentate bridging mode while in the squarates $M(C_4O_4)\cdot 4H_2O$ ($M = Mn^{2+}$, Fe^{2+}, Co^{2+}, Ni^{2+}, and Zn^{2+}) synthesized by Weiss et al.,[1f] the ligand bridges adjacent metal atoms μ-1,3 along the polymeric chains. Interposition of the squarate rings between neighboring metal atoms in cis-bismonodentate and trismondentate modes has been observed in a series of lanthanide(III) squarates studied by Petit et al.[1n] In a set of lanthanide(III)−copper(II) squarates prepared by Bouayad et al.,[1p] the ligand adopts both trismonodentate and trans-bismonodentate coordination, while the copper(II) squarates studied by Solans et al.[3f] contain μ-1,2-squarato-bridged copper(II) units. The mixed-valence vanadium complexes prepared by Khan et al.[1q] contain μ-1,2- and μ-1,3-squarate bridges.

However, in lead(II) squarate and all the lead(II) aminosquarates characterized so far with the exception of $Pb[(C_2H_5)_2NC_4O_3]_2(H_2O)$ (**2**), the ligands always complex in a cis-monodentate fashion with the lead atoms linearly arranged when viewed along the polymeric chains. The intervening twisted oxygen bridges cause the neighboring lead atoms to zigzag, and the result is the existence of parallel chains. In $Pb[(C_2H_5)_2NC_4O_3]_2(H_2O)$ (**2**) the ligand complexes both bidentate and trismonodentate. The almost orthogonal orientation of the adjacent Pb_2O_2 rings in this complex appears responsible for the ligand utilizing its three oxygen atoms in coordinating to three neighboring lead atoms simultaneously. The arrangement of the oxo-bridged lead atoms such that there is no intervention of μ-1,3- or tetrakismonodentate ligand bridges between juxtaposed lead atoms is an interesting feature of these complexes.

The intrachain Pb···Pb distances for complexes **1**−**3** and lead(II) aminosquarate range from 4.30 to 4.52 Å (Table 8). These distances are short compared to the intramolecular Cu···Cu distance of 5.21 Å in $Cu_2(salNEt_2)_2(H_2O)(C_4O_4)\cdot H_2O$,[3g] a μ-1,2-squarato-bridged Cu(II) complex which has a large antiferromagnetic interaction. Strong antiferromagnetic effects were also observed in the vanadium(IV) complex $NH_4[V_2O_2(OH)(C_4O_4)_2(H_2O)_3]H_2O$,[1q] which has the squarate ligand cis-monodentate and bridging OH groups. The short V···V distance of 3.33 Å, the bridging hydroxo groups, and the presence of localized

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[6] (a) Lehn, J.-M. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 1304. (b) Zerkowski, J. A.; Seto, C. T.; Wierda, D. A.; Whitesides, G. M. *J. Am. Chem. Soc.* **1990**, *112*, 9025. (c) Zerkowski, J. A.; Christopher, T. S.; Whitesides, G. M. *J. Am. Chem. Soc.* **1992**, *114*, 5473.

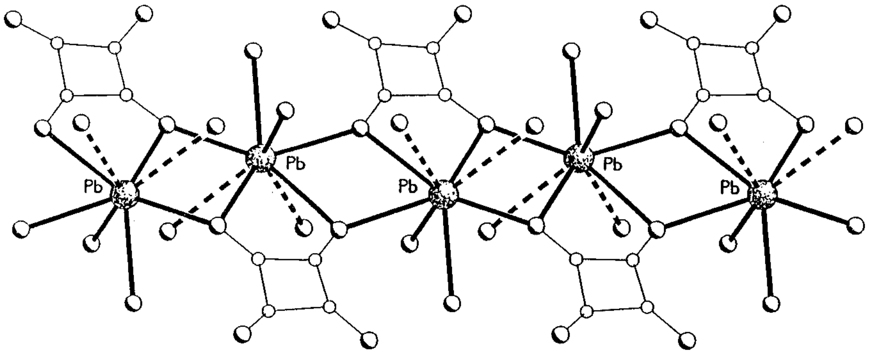

Figure 6. Part of one of the O-bridged and H-bonded polymeric ribbons in the structure of **3**.

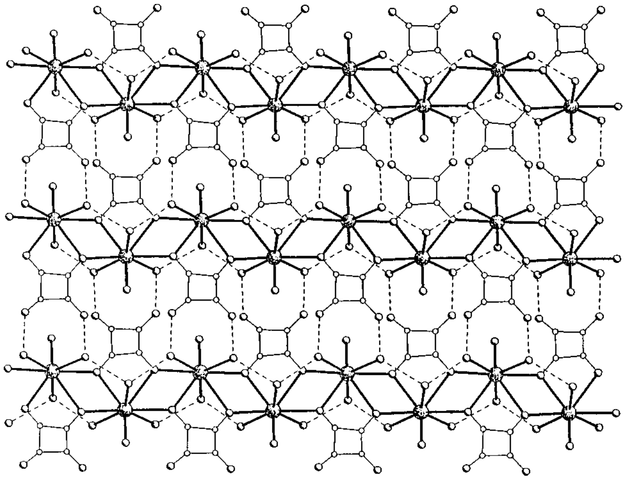

Figure 7. Part of one of the corrugated sheets in the structure of **3**.

Table 8. Pb···Pb Distances (Å) for Lead(II) Squarate and Lead(II) 1-(Dialkylamino)squarates

complex	Pb···Pb distance (Å)
$Pb(C_4O_3HNH_2)_2(OH_2)_2$	4.30, 4.32
$Pb(C_4O_4)(H_2O)_4$ (**3**)	4.44
$Pb[(CH_3)_2NC_4O_3]_2(OH_2)_2 \cdot H_2O$ (**1**)	4.32, 4.34
$Pb[(C_2H_5)_2NC_4O_3]_2(H_2O)$ (**2**)	4.43, 4.52

squarate ring bonds were assumed responsible for the magnitude of the magnetic exchange. However, it has been shown that only weak exchange interactions are possible with μ-1,3- and tetrakismonodentate bridging. Such weak interactions were observed in a series of copper(II) squarates studied by Solans et al.[3f] and were shown to be due to the weak overlap between the copper orbitals and the bridging ligand orbitals.

The prerequisites for proper overlap and hence magnetic exchange have therefore been suggested as being the existence of the ligand in a localized form, short metal–metal distances, and bridging oxo or hydroxo groups. Unfortunately, it is not possible to compare the C–C bond lengths in the C_4 cycles in the lead complexes because the heavy lead atoms limit the accuracy with which these can be determined. We, therefore, cannot say if multiple-bond localization occurs in these complexes.

Conclusion

Preparation of transition metal complexes analogous to the lead(II) complexes with similar arrangements of metal atoms seems feasible. These transition metal aminosquarate and 1-(dialkylamino)squarate complexes with structures similar to the lead(II) complexes should possess the requisite characteristics necessary to facilitate antiferromaganetic interactions and the other phenomena referred to previously (vide supra).

Supporting Information Available: Figures S1–S3, showing the asymmetric units, Table S1, listing experimental data (^{1}H NMR, yields, and elemental analyses), and Tables S2–S12, listing crystal and structural refinement data, anisotropic displacement parameters, hydrogen atom coordinates, and complete sets of bond lengths and angles (15 pages). Ordering information is given on any current masthead page.

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