tronic absorption bands appear as one consequence of the electronic coupling. The gain or loss of electrons involves delocalized molecular levels and the formation of delocalized mixed-valence ions.

The 4+ and 5+ ions are the dimeric analogues of ruthenium-red, $[(NH_3)_5RuORu(NH_3)_4RuORu(NH_3)_5]^{6+}$, and ruthenium-brown, $[(NH_3)_5RuORu(NH_3)_4ORu(NH_3)_5]^{7+}$, which themselves may be members of a chemically accessible set of higher oligomers.[25] Although it is not our intention to make detailed comparisons in this paper, it is interesting to note that the effect of increased number of interacting ions is what would might have been expected intuitively. For example, for the lowest energy, intense absorption band, λ_{max} is at 503 nm for the 4+ dimer and at 532 nm for Ru-red.

Another comparison of interest is between the decaammine dimers and the analogous bpy dimers like $[(bpy)_2ClRuORuCl(bpy)_2]^{3+/2+}$ where the Ru–O–Ru interaction is presumably somewhat modified by changes in the nonbridging ligands.[2] From the comparison of the [3,3] dimers $[(NH_3)_5RuORu(NH_3)_5]^{4+}$ and $[(bpy)_2ClRuORuCl(bpy)_2]^{2+}$, both apparently have similar ground states, probably similar structures, and stable, delocalized [3,4] ions. The low-energy optical spectra of both the [3,3] and [3,4] ions are dominated by what appear to be $\pi^* \leftarrow \pi^n$, d_{xy} transitions which are at significantly lower energies for the bpy dimers: 672 nm for $[(bpy)_2ClRuOCl(bpy)_2]^{2+}$ and 470 nm for $[(bpy)_2ClRuORuCl(bpy)_2]^{3+}$. In the context of the MO diagram in Figure 3, the smaller π^*–$d\pi^n$ energy gap suggested by the spectral results also suggests that the extent of Ru–O–Ru electronic coupling is less for the bpy dimers. Also by use of Figure 3, comparative values of redox potentials suggest that the π_1^*, π_2^* levels are at higher energy for the decaammine system, making it easier to oxidize. In both cases, the potentials for oxidation to a high formal oxidation state [Ru(IV)] are remarkably low, apparently due to the extensive destabilization of the highest, largely $d\pi$(Ru) levels due to the Ru–O–Ru interaction. The relatively low potential for reduction of $[(bpy)_2ClRuORuCl(bpy)_2]^{2+}$ may have its origin in strong mixing by configurational interaction between the π^* levels and low-lying, vacant π^* levels on the 2,2′-bipyridyl ligands.

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Registry No. 1, 18532-87-1; **2a**, 34843-18-0; **2b**, 72049-59-3; **3a**, 72049-57-1; **3c**, 72049-55-9; **4a**, 72186-96-0; **4b**, 72186-95-9; **5**, 72049-54-8; **6**, 72186-94-8.

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Contribution from the Miami Valley Laboratories,
The Procter & Gamble Company, Cincinnati, Ohio 45247

Structural Investigations of Calcium-Binding Molecules. 5. Structure Analysis of a Calcium Salt of Benzenehexacarboxylic Acid (Mellitic Acid), $Ca_2C_{12}H_2O_{12}\cdot 9H_2O$

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The crystal and molecular structure of dicalcium dihydrogen mellitate nonahydrate was determined by three-dimensional X-ray crystal structure analysis using a combination of direct and heavy-atom methods. $Ca_2C_{12}H_2O_{12}\cdot 9H_2O$ crystallizes in orthorhombic space group $P2_12_12_1$ with $a = 6.825(2)$ Å, $b = 16.615(5)$ Å, and $c = 18.857(6)$ Å and four formula units per unit cell. Block-diagonal least-squares refinement using automated diffractometer-collected data resulted in $R_1 = 7.8\%$ and $R_2 = 4.8\%$. The crystal structure consists of an extended network of calcium ion coordinated mellitate acid anions and water molecules linked by a complex hydrogen-bonding network. The mellitate acid anions have the two acid hydrogen atoms on meta-related carboxyl groups and are linked together by strong (2.465 and 2.530 Å) intermolecular hydrogen bonds. The two independent calcium ions are seven- and eight-coordinate, respectively. The primary binding between the calcium ions and the mellitate ion is through the formation of four-membered chelate rings utilizing bidentate carboxylate groups. Equilibrium binding constants between Ca^{2+} and mellitate^{6-} were determined via potentiometric titrations utilizing a calcium ion selective electrode. The data could be best fit by the following concentration constants (25 °C, ionic strength 0.1 M KCl): $K_{11} = (3.05 \pm 0.15) \times 10^3$ (mol·L)$^{-1}$ and $K_{21} = (0.37 \pm 0.03) \times 10^3$ (mol·L)$^{-1}$.

Introduction

A continuing program of structural investigations of calcium salts has sought to determine characteristics of calcium binding and to relate solid-state properties (as revealed by single-crystal X-ray analysis) of calcium complexes to behavior in aqueous solution. In part, the purpose of these studies is derived from the considerable interest in finding environmentally innocuous alternatives to polyphosphates for calcium sequestration. Polycarboxylic acids such as benzenehexacarboxylic acid (or salts thereof), otherwise known as mellitic acid, have been suggested[1] as such phosphorus-free nitrogen-free alternatives. Recent studies have also indicated that in an ionized state mellitic acid can function as a crystal growth inhibitor in calcium phosphate precipitation reactions.[2] A determination of the crystal and molecular structure of a calcium salt of mellitic acid was thus viewed as important in the calcium coordination studies being undertaken in our laboratories. Other studies discussed below have indicated a rather stable aqueous complexation between Ca^{2+} and the mellitate anion, $C_{12}O_{12}{}^{6-}$. It is of particular interest to us to know how Ca^{2+} might bind to a polycarboxylate ligand which does not have the capability for five- or six-membered chelate ring formation (which is traditionally implicated in stable complex formation).

Previously the crystal structure of the parent mellitic acid was reported by Darlow.[3] Also, a recent report on the ionization of polycarboxylic acids, including mellitic acid, has appeared.[4] To our knowledge, there has been only one other

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(1) Japanese Patent No. 4709984; Great Britian Patent No. 1317076.

(2) M. D. Francis, C. L. Slough, W. W. Briner and R. P. Oertel, *Calcif. Tissue Res.*, **23**, 53 (1977).

(3) S. F. Darlow, *Acta Crystallogr.*, **14**, 159 (1961).

published report of a structural study of calcium binding with a benzenepolycarboxylate; this is the crystal structure of calcium terephthalate trihydrate.[5]

Experimental Section

Preparation of $Ca_2C_{12}H_2O_{12}\cdot 9H_2O$. Crystals of $Ca_2C_{12}H_2O_{12}\cdot 9H_2O$ suitable for single-crystal X-ray analysis were obtained by slow evaporation at room temperature of a solution 0.25 M in $CaCl_2$ and 0.025 M in mellitic acid; the pH of the solution was unadjusted. The crystalline material was separated from the mother liquor by filtration, washed with water, and dried in air. The rod-shaped crystals are only sparingly soluble in water. The compound gave a satisfactory elemental analysis which was confirmed by the crystal structure determination. $CaCl_2$ was Mallinckrodt Analytical Reagent; mellitic acid was used as obtained from Pfaltz and Bauer, Inc.

X-ray Data Collection. A rod-shaped single crystal of $CaC_{12}H_2O_{12}\cdot 9H_2O$ having dimensions 0.10 × 0.125 × 0.45 mm (rotation *a* axis) was mounted with epoxy cement on a thin glass fiber. Preliminary oscillation, Weissenberg, and precession X-ray photographs indicated orthorhombic symmetry. The crystal was optically aligned on a Siemens automated single-crystal diffractometer and 25 diffraction maxima were manually centered. Lattice constants were obtained (at 25 °C) by least-squares refinement of the measured θ settings of these reflections. These lattice constants were used to generate diffractometer angle settings for all data reflections. The method of data collection was identical with a previously reported procedure.[6] A total of 3575 independent intensities for which $2\theta \leq 60°$ (Mo Kα radiation; graphite monochromator) was collected from the *hkl* octant. Of these data, 2711 amplitudes with net intensity greater than 3 times the standard deviation of the background intensity were considered to be observed. No absorption or extinction corrections were applied. The linear absorption coefficient (μ) of 5.02 cm^{-1} for Mo Kα radiation results in a $\mu R_{max} \leq 0.2$ for which the change of absorption correction factors with θ is negligible. The effects of absorption result in extremes for the I/I_0 ratio of 0.82 and 0.95. Thus a reflection of measured intensity 1.0 could vary in intensity from 1.22 to 1.05, i.e., a variation of less than 8% about the mean value. The scattering factors used for all atoms except Ca^{2+} were those compiled by Hanson et al.[7] Ca^{2+} scattering factors were obtained from ref 8.

Unit Cell and Space Group. Lattice constants (25 °C) and their estimated standard deviations for this orthorhombic crystal of $Ca_2C_{12}H_2O_{12}\cdot 9H_2O$ are $a = 6.825$ (2) Å, $b = 16.615$ (5) Å, and $c = 18.857$ (6) Å; unit cell volume is 2138.6 Å^3. These lattice constants were used in all calculations. The experimental density of 1.80 ± 0.01 g cm^{-3} (determined by flotation in mixtures of ethylene dichloride and ethylene dibromide) agrees well with the value of 1.81 calculated on the basis of four formula species per unit cell. The total number of electrons per unit cell, $F(000)$, is 1200. Systematic absences of h odd for (h00), k odd for (0k0), and l odd for (00l) uniquely define the probable space group as $P2_12_12_1$ (D_2^4, No. 19). The assignment of this space group was verified by the successful refinement of the structure in this space group. The solution of the structure required the location of 2 calcium, 21 oxygen, 12 carbon, and, ideally, 20 hydrogen atoms, corresponding to one formula unit per unit cell. The crystallographically independent atoms were each found from the structural analysis to occupy the general fourfold set of positions: x, y, z; $^1/_2 - x, \bar{y}, {}^1/_2 + z$; $^1/_2 + x, {}^1/_2 - y, \bar{z}$; $\bar{x}, {}^1/_2 + y, {}^1/_2 - z$.

Table I. Final Atomic Positional Parameters with Their Standard Deviations for $Ca_2C_{12}H_2O_{12}\cdot 9H_2O$

	x ($10^4\sigma$)	y ($10^4\sigma$)	z ($10^4\sigma$)
Ca(1)	0.1564 (3)	0.2981 (1)	0.4601 (1)
Ca(2)	0.0963 (3)	0.6960 (1)	0.4734 (1)
C(1)	0.5943 (12)	0.5696 (4)	0.3342 (3)
C(2)	0.5982 (13)	0.5701 (4)	0.4092 (3)
C(3)	0.6202 (12)	0.4974 (4)	0.4464 (3)
C(4)	0.6357 (11)	0.4239 (4)	0.4104 (3)
C(5)	0.6332 (11)	0.4235 (4)	0.3370 (3)
C(6)	0.6118 (12)	0.4948 (4)	0.2987 (3)
C(7)	0.5815 (13)	0.6473 (4)	0.2951 (3)
C(8)	0.5952 (11)	0.6492 (4)	0.4482 (3)
C(9)	0.6237 (13)	0.5023 (4)	0.5275 (3)
C(10)	0.6476 (11)	0.3466 (4)	0.4540 (4)
C(11)	0.6624 (12)	0.3444 (4)	0.2945 (4)
C(12)	0.6045 (13)	0.4926 (4)	0.2185 (3)
O(1)	0.4292 (9)	0.6567 (3)	0.2563 (3)
O(2)	0.7178 (9)	0.6974 (3)	0.3008 (3)
O(3)	0.4348 (8)	0.6828 (3)	0.4579 (3)
O(4)	0.7569 (8)	0.6767 (3)	0.4712 (3)
O(5)	0.4840 (9)	0.5321 (3)	0.5589 (3)
O(6)	0.7776 (9)	0.4701 (1)	0.5563 (3)
O(7)	0.4952 (8)	0.3231 (3)	0.4851 (3)
O(8)	0.8090 (8)	0.3084 (3)	0.4573 (3)
O(9)	0.5494 (9)	0.2840 (3)	0.3171 (3)
O(10)	0.7771 (11)	0.3414 (3)	0.2454 (3)
O(11)	0.4723 (10)	0.4569 (4)	0.1881 (3)
O(12)	0.7394 (9)	0.5333 (3)	0.1869 (3)
O(13)	0.1541 (9)	0.4213 (3)	0.3979 (3)
O(14)	0.1459 (11)	0.2265 (4)	0.3527 (3)
O(15)	0.3706 (10)	0.3284 (3)	0.1022 (3)
O(16)	0.9285 (9)	0.1364 (3)	0.1466 (3)
O(17)	0.9293 (10)	0.3042 (3)	0.1130 (3)
O(18)	0.8762 (9)	0.0483 (3)	0.0041 (3)
O(19)	0.8725 (11)	0.1060 (3)	0.3292 (3)
O(20)	0.1146 (11)	0.4441 (4)	0.2562 (4)
O(21)	0.6058 (11)	0.1317 (3)	0.4322 (3)

Determination of Structure. A Patterson map was calculated and the positional parameters of the two independent calcium atoms were sought from analysis of Harker peaks, but a solution was not evident. Therefore a two-dimensional direct-methods approach was attempted which utilized 491 reflections of the centrosymmetric 0kl projection. Normalized structure factor magnitudes, $|E|$, were obtained, and three symbols were used in the symbolic addition phase determination procedure. From this procedure 92 symbolic phases were determined with $|E| > 1.10$; the phases of two of the three symbols were indicated. Two 0kl E-map projections were calculated and two large peaks appeared in each map. A comparison with the peaks in the Patterson map suggested the correct choice of E maps and therefore the y and z coordinates of the two calcium ions. Further examination of the E-map projection revealed the y and z coordinates of all nonhydrogen atoms of the mellitate anion. Fortunately the ring lies in a plane perpendicular to the a axis and could thus be readily identified in the 0kl projection. The x coordinates were determined from an examination of the Patterson map. A consideration of the coordinates of the calcium ions indicates the reasons for the initial problems in interpretation of the Patterson map. The two crystallographically independent calcium ions are related by the pseudosymmetry of nearly equal x coordinates, nearly equal z coordinates, and y coordinates approximately related by a change of sign (see Table I). These coordinate relationships resulted in a nearly complete overlap of the three Harker peaks resulting from the two calcium ions. The positional coordinates of the remaining nonhydrogen atoms (i.e., nine water molecule oxygen atoms) were found by difference density calculations. Block-diagonal least-squares calculations were used to refine the positional coordinates and anisotropic thermal parameters to final discrepancy factors of

$$R_1 = [\Sigma||F_o| - |F_c||/\Sigma|F_o|] \times 100 = 7.8\%$$

$$R_2 = [\Sigma w||F_o| - |F_c||^2/\Sigma w|F_o|^2]^{1/2} \times 100 = 4.8\%$$

Refinement was based on the minimization of $\sum w_i \Delta F_i^2$ and weights were determined according to the relationship $w_i = 1/\sigma_i^2(F_o)$. A final difference density calculation contained no irregularities and also did not allow the unequivocal identification of hydrogen atom positions.

Final atomic positional and anisotropic thermal parameters and structure factor amplitudes are given in Tables I, A-I, and A-II, respectively; Table II lists interatomic distances and angles.[9]

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(9) Data reduction and direct-methods procedures were carried out by using locally written programs for IBM 1800 and 360-44 computers. Fourier calculations were carried out by using a locally modified version of the University of Wisconsin Fourier program and block-diagonal least-squares refinements were calculated by using a program obtained from Professor R. E. Davis, University of Texas.

Table II. Interatomic Distances and Angles and Their Standard Deviations for $Ca_2C_{12}H_2O_{12}\cdot 9H_2O$[a]

A. Calcium Coordination			
Ca(1)···O(7)	2.403 (6)	Ca(2)···O(3)	2.347 (6)
Ca(1)···O(8)[b]	2.385 (6)	Ca(2)···O(4)[b]	2.346 (6)
Ca(1)···O(7)[c]	2.516 (5)	Ca(2)···O(3)[d]	2.635 (5)
Ca(1)···O(8)[c]	2.576 (5)	Ca(2)···O(4)[d]	2.601 (5)
Ca(1)···O(13)	2.357 (5)	Ca(2)···O(15)[e]	2.472 (5)
Ca(1)···O(14)	2.349 (6)	Ca(2)···O(16)[f]	2.473 (5)
Ca(1)···O(21)[c]	2.368 (6)	Ca(2)···O(17)[f]	2.430 (5)
		Ca(2)···O(18)[f]	2.494 (5)
B. Bonding Distances for Ligands			
C(1)–C(2)	1.414 (10)	C(7)–O(1)	1.284 (10)
C(2)–C(3)	1.403 (10)	C(7)–O(2)	1.255 (10)
C(3)–C(4)	1.400 (10)	C(8)–O(3)	1.245 (9)
C(4)–C(5)	1.384 (9)	C(8)–O(4)	1.274 (9)
C(5)–C(6)	1.394 (9)	C(9)–O(5)	1.230 (10)
C(6)–C(1)	1.415 (10)	C(9)–O(6)	1.301 (10)
av C_r–C_r[k]	1.402	C(10)–O(7)	1.259 (9)
C(1)–C(7)	1.487 (10)	C(10)–O(8)	1.276 (9)
C(2)–C(8)	1.506 (9)	C(11)–O(9)	1.336 (9)
C(3)–C(9)	1.531 (9)	C(11)–O(10)	1.215 (10)
C(4)–C(10)	1.526 (9)	C(12)–O(11)	1.225 (10)
C(5)–C(11)	1.551 (9)	C(12)–O(12)	1.291 (10)
C(6)–C(12)	1.513 (9)		
av C_r–C_c[k]	1.519		
C. Bond Angles for Ligand			
C(6)–C(1)–C(2)	118.4 (6)	O(1)–C(7)–C(1)	115.8 (7)
C(3)–C(2)–C(1)	119.8 (6)	O(2)–C(7)–C(1)	119.2 (7)
C(4)–C(3)–C(2)	120.9 (6)	O(3)–C(8)–C(2)	118.3 (7)
C(5)–C(4)–C(3)	119.2 (6)	O(4)–C(8)–C(2)	117.8 (7)
C(4)–C(5)–C(6)	121.0 (6)	O(5)–C(9)–C(3)	119.4 (7)
C(5)–C(6)–C(1)	120.6 (6)	O(6)–C(9)–C(3)	114.1 (7)
av C_r–C_r–C_r[k]	120.0	O(7)–C(10)–C(4)	117.8 (7)
C(7)–C(1)–C(6)	122.1 (6)	O(8)–C(10)–C(4)	119.4 (7)
C(7)–C(1)–C(2)	119.4 (6)	O(9)–C(11)–C(5)	113.3 (6)
C(8)–C(2)–C(3)	120.4 (6)	O(10)–C(11)–C(5)	120.8 (7)
C(8)–C(2)–C(1)	119.6 (6)	O(11)–C(12)–C(6)	120.3 (7)
C(9)–C(3)–C(4)	121.9 (6)	O(12)–C(12)–C(6)	115.2 (7)
C(9)–C(3)–C(2)	117.1 (6)	av O–C_c–C_r	117.6
C(10)–C(4)–C(3)	118.4 (6)	O(1)–C(7)–O(2)	125.0 (6)
C(10)–C(4)–C(5)	122.3 (6)	O(3)–C(8)–O(4)	123.8 (6)
C(11)–C(5)–C(4)	121.3 (6)	O(5)–C(9)–O(6)	126.5 (6)
C(11)–C(5)–C(6)	117.6 (6)	O(7)–C(10)–O(8)	122.8 (6)
C(12)–C(6)–C(1)	119.4 (6)	O(9)–C(11)–O(10)	125.9 (7)
C(12)–C(6)–C(5)	120.1 (6)	O(11)–C(12)–O(12)	124.5 (6)
av C_r–C_r–C_c[k]	120.0	av O–C–O	124.7
D. Probable Hydrogen Bond Distances			
O(6)···O(12)[g]	2.465 (7)	O(9)···O(14)	2.999 (9)
O(1)···O(9)[f]	2.530 (7)	O(10)···O(17)	2.775 (8)
O(1)···O(19)[f]	2.752 (9)	O(10)···O(20)[i]	2.879 (10)
O(1)···O(16)[f]	3.077 (8)	O(11)···O(15)	2.767 (8)
O(2)···O(14)[f]	3.078 (7)	O(11)···O(20)	2.774 (10)
O(2)···O(15)[f]	2.904 (7)	O(13)···O(20)	2.712 (8)
O(5)···O(18)[f]	2.750 (8)	O(13)···O(18)[f]	2.809 (7)
O(5)···O(17)[g]	2.960 (7)	O(14)···O(19)[b]	2.775 (9)
O(6)···O(21)[h]	2.820 (9)	O(19)···O(21)	2.698 (9)
E. Some Nonbonding Distances			
O(1)···O(2)	2.251 (8)	C(7)···C(8)	2.888 (9)
O(3)···O(4)	2.223 (8)	C(9)···C(10)	2.935 (10)
O(5)···O(6)	2.259 (8)	C(7)···C(12)	2.950 (10)
O(7)···O(8)	2.225 (8)	C(9)···C(8)	2.866 (10)
O(9)···O(10)	2.272 (9)	C(10)···C(11)	3.008 (9)
O(11)···O(12)	2.226 (9)	C(11)···C(12)	2.873 (10)
Ca(1)···Ca(1)[h]	4.065 (2)	Ca(1)···Ca(1)[c]	4.065 (2)
Ca(2)···Ca(2)[j]	3.992 (2)	Ca(2)···Ca(2)[d]	3.992 (2)

[a] Distances are in angstroms and angles in degrees; standard deviation of the last significant figure is given in parentheses. [b] Related to atomic position in Table I by following symmetry operation: $-1 + x, y, z$. [c] $-\frac{1}{2} + x, \frac{1}{2} - y, 1 - z$. [d] $-\frac{1}{2} + x, 1\frac{1}{2} - y, 1 - z$. [e] $\frac{1}{2} - x, 1 - y, \frac{1}{2} + z$. [f] $1 - x, \frac{1}{2} + y, \frac{1}{2} - z$. [g] $1\frac{1}{2} - x, 1 - y, \frac{1}{2} + z$. [h] $\frac{1}{2} + x, \frac{1}{2} - y, 1 - z$. [i] $1 + x, y, z$. [j] $1\frac{1}{2} + x, 1\frac{1}{2} - y, 1 - z$. [k] Key: C_r = ring carbon; C_c = carboxyl carbon.

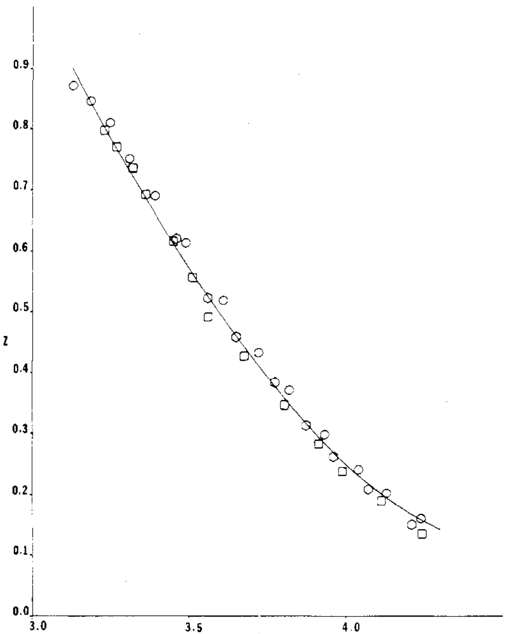

Figure 1. Z vs. log [Ca^{2+}], 25 °C, IS = 0.1 M (KCl): $C_{\text{mellitate}} = 1.0 \times 10^{-3}$ M (circle); 0.5×10^{-3} M (square); 0.25×10^{-3} M (hexagon). Curve is calculated with assumed stability constants: $K_{11} = 3.05 \times 10^3$, $K_{21} = 0.37 \times 10^3$.

Determination of Calcium Mellitate Stability Constants. The stability constants for calcium mellitate interactions were determined from data obtained by potentiometric titrations using an Orion Model 92-20 calcium ion selective electrode, a calomel glass sleeve reference electrode, and a Corning Model 12 expanding scale pH meter. Titrations were carried out at 25 °C with magnetic stirring in a covered cell under a blanket of nitrogen. In order to maintain a relatively constant ionic strength, we made both titrant and titrand 0.1 M in potassium chloride. The pH was held constant at 8.5 (using potassium hydroxide) in order to ensure the absence of any significant amounts of protonated mellitate species (pK_6 for mellitic acid = 7.49), as well as to minimize interference from carbonate (pK_2 for carbonic acid = 10.25). Stock solutions of calcium chloride were freshly prepared by dissolving reagent grade analytical standard calcium carbonate in a solution of hydrochloric acid, neutralizing with potassium hydroxide, and then boiling the solution to drive off carbonate as CO_2. Aliquots of this solution were used for titrations as well as for standardization of the calcium ion electrode; a standard Ca^{2+} concentration vs. emf curve (Figure A-1) was obtained at the pH and ionic strength conditions and over the range of concentrations encountered during the titrations ($(5-100) \times 10^{-5}$ M $C_{Ca^{2+}}$). Only data which fell in the linear region of these curves were used. The titrations were performed by addition of a calcium ion solution to a solution of mellitate, with addition of mellitate to maintain a constant total mellitate ion concentration. A "sandwich" experimental design was used; i.e., emf's of the standard calcium solutions were determined between calcium–mellitate titrations; these emf values were used to generate the standard Ca^{2+} concentration vs. emf curves. A local Fortran version of the program LETAGROPVRID[10] was used for reduction of the titration data to stability constants; a procedure similar to one previously reported by Grabenstetter and Cilley[11] was followed. Replicate runs were made at each of three constant mellitate concentrations (0.25, 0.5, and 1.0 mM) and values of each point averaged. The titration data were well fit (Figure 1) by assuming the following stability constants: $K_{11} = (3.05 \pm 0.15) \times 10^3$ (mol·L)$^{-1}$ and $K_{21} = (0.37 \pm 0.03) \times 10^3$ (mol·L)$^{-1}$, where K_{11} and K_{21} are for the complexes Ca(mellitate)$^{4-}$ and Ca_2(mellitate)$^{2-}$, respectively; the errors given are 3 times the standard deviation generated by the LETAGROPVRID program; this standard deviation is based on the least-squares fit between data points input and calculated from estimated stability constants. No attempt was made to include higher order complexes

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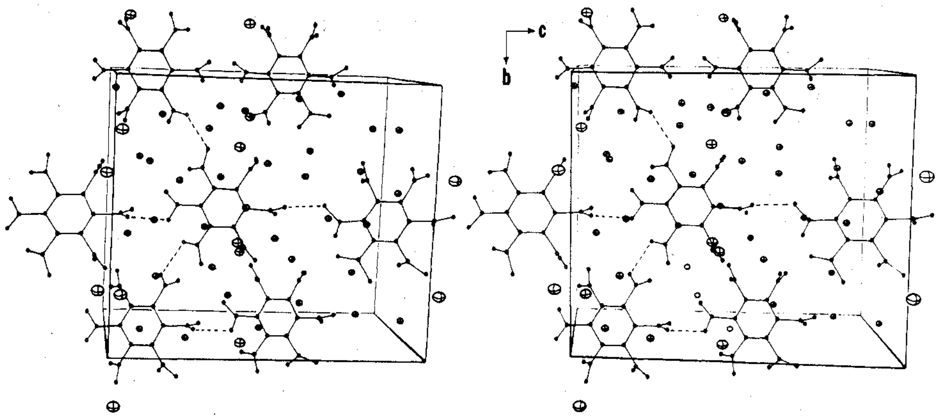


Figure 2. Stereographic crystal packing diagram of Ca_2H_2mellitate·$9H_2O$ placed on orthorhombic unit cell axes (positive *a* axis directed toward viewer).

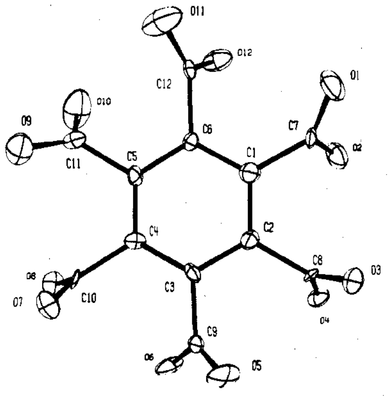


Figure 3. H_2mellitate^{4-} acid anion.

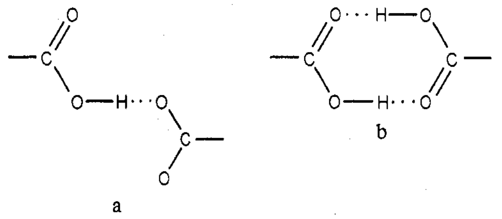
in the calculations. These values are concentration constants for the ionic strength conditions given above and are uncorrected for activities. Table A-III gives titration data including $[Ca^{2+}]$ and the average number of Ca^{2+} ions bound per ligand.

All chemicals were reagent grade and used as received. Mellitic acid for these experiments was obtained from Fluka AG. pH titrations indicated a purity level of 99%.

Results and Discussion

The crystal structure of dicalcium dihydrogen mellitate nonahydrate (Ca_2H_2mellitate·$9H_2O$) (Figure 2) consists of H_2mellitate acid anions (Figure 3), which lie in planes nearly perpendicular to the unit cell *a* axis and which are linked together by coordination to calcium ions and by strong hydrogen bonds between carboxyl and carboxylate groups of adjacent acid anions. Each of the two meta carboxylate ions forms a chelate ring with one of the calcium ions. Each oxygen of these carboxylate groups is also coordinated with the other calcium ion to form spirals about the twofold screw axes parallel to the *a* axis, as shown in Figure 4. Water molecules are distributed about the crystal structure; seven of the nine independent water molecules are involved in coordination with the calcium ions and all but one of the water molecules are involved with the mellitate acid anions in a complex hydrogen bond network. Of the mellitate oxygen atoms, only those coordinated to calcium ions are not involved in this network.

The layered arrangement of mellitate acid anions is similar to that found in the crystal structure of mellitic acid.[3] However, in the calcium salt described here, the intermolecular hydrogen bonding is between carboxyl and carboxylate groups (a) rather than between carboxyl groups (b). Interatomic



distances and angles (Table II) of the mellitate acid anion (Figure 3) are within the ranges of values of previously de-

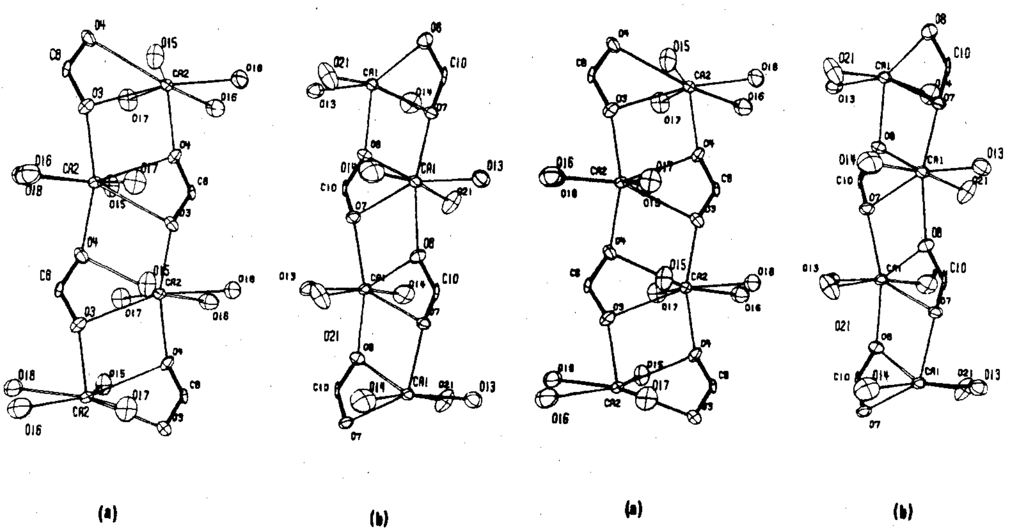


Figure 4. Stereographic views of Ca^{2+} coordination environments: (a) Ca(2); (b) Ca(1).

Table III. Equation of Least-Squares Planes and Distances (Å) from These Planes[a]

A. Plane Containing C(1), C(2), C(3), C(4), C(5), and C(6)

$0.9941X + 0.1064Y - 0.0202Z - 4.9122 = 0$

C(1)	−0.0008	C(7)	0.0648
C(2)	−0.0016	C(8)	0.1026
C(3)	0.0051	C(9)	0.0061
C(4)	−0.0061	C(10)	−0.0785
C(5)	0.0038	C(11)	0.0788
C(6)	−0.0004	C(12)	−0.0233

B. Plane Containing C(1), C(2), C(3), C(4), C(5), C(6), C(7), C(8), C(9), C(10), C(11), and C(12)

$0.9955X + 0.00930Y - 0.0169Z - 4.8435 = 0$

C(1)	−0.0321	O(1)	−0.9944
C(2)	−0.0283	O(2)	1.0157
C(3)	−0.0031	O(3)	−0.9801
C(4)	−0.0001	O(4)	1.1951
C(5)	0.0055	O(5)	−0.9111
C(6)	−0.0171	O(6)	0.9889
C(7)	0.0138	O(7)	−1.1345
C(8)	0.0608	O(8)	0.9841
C(9)	0.0019	O(9)	−0.7727
C(10)	−0.0525	O(10)	0.8857
C(11)	0.0956	O(11)	−0.9881
C(12)	−0.0445	O(12)	0.9451
		Ca(1)	−0.2439
		Ca(2)	0.2824

C. Plane Containing C(10), O(7), and O(8)

$-0.2578X - 0.5284Y - 0.8089Z + 11.1068 = 0$

Ca(1)	−0.0566

D. Plane Containing C(8), O(3), O(4)

$0.1207X + 0.5130Y - 0.8498Z - 1.1584 = 0$

Ca(2)	0.0634

E. Plane Containing C(10), O(13), O(14), O(21)

$0.9983X - 0.0211Y - 0.0536Z - 3.7305 = 0$

C(10)	0.1020	Ca(1)	0.1256
O(13)	0.0905	O(7)	−0.9600
O(14)	−0.0793	O(8)	1.2117
O(21)	−0.0857	O(7)′	2.4679
		O(8)′	−2.2405

F. Plane Containing C(8), O(15), O(16), O(17), O(18)

$-0.9954X + 0.0468Y - 0.0832Z + 4.2628 = 0$

C(8)	0.0213	Ca(2)	0.0113
O(15)	0.0072	O(3)	1.1219
O(16)	0.0381	O(4)	−1.0924
O(17)	−0.0350	O(3)′	−2.3027
O(18)	−0.0258	O(4)′	2.3281

[a] The Smith least-squares plane program [D. L. Smith, Ph.D. Thesis (Appendix), University of Wisconsin (Madison), 1962] was used to obtain the equations of best planes formed by atoms indicated and also the perpendicular distances of these and other atoms from the planes. The equation of the least-squares plane is expressed in orthogonal coordinates X, Y, Z, which are related to cell coordinates by the transformation: $X = ax + b(\cos\gamma)y + c(\cos\beta)z$; $Y = [b(1 - \cos^2\gamma)^{1/2}]y + [c(\cos\alpha - \cos\beta - \cos\gamma)/(1 - \cos^2\gamma)^{1/2}]z$; $Z = c[1 - \cos^2\beta - (\cos\alpha - \cos\beta\cos\gamma)^2 \sin^2\gamma]^{1/2}z$. The least-squares plane equation is written as $M(1)X + M(2)Y + M(3)Z - D = 0$, where M(1), M(2), and M(3) are the components of a unit vector normal to the best plane, and D is the perpendicular distance fromthe plane to origin.

Table IV. Angles (Deg) between Perpendiculars of Planes

plane 1	plane 2	angle
C_6 ring	C(7) carboxyl	63.8
C_6 ring	C(8) carboxyl	78.9
C_6 ring	C(9) carboxyl	56.7
C_6 ring	C(10) carboxyl	72.8
C_6 ring	C(11) carboxyl	47.5
C_6 ring	C(12) carboxyl	61.3
C_6 ring	C(10), O(13), O(14), O(21)	7.6
C_6 ring	C(8), O(15), O(16), O(17), O(18)	169.4

Table V. Angles (Deg) between Perpendiculars of Planes and Vectors

plane	vector	angle
C_6 ring	*a* axis	6.2
C(10), O(13), O(14), O(21)	Ca(1)–O(7)′	167.9
C(10), O(13), O(14), O(21)	Ca(1)–O(8)′	5.7
C(8), O(15), O(16), O(17), O(18)	Ca(2)–O(3)′	8.4
C(8), O(15), O(16), O(17), O(18)	Ca(2)–O(4)′	172.2

termined benezenecarboxylic acids and carboxylates;[12] best-planes of atoms are given in Table III. The carboxyl and carboxylate groups all make relatively large dihedral angles (Table IV) with the C_6 ring; the two calcium ion coordinated carboxylate groups exhibit dihedral angles closest to 90° (i.e., perpendicular to plane of C_6 ring). This relative arrangement of CO_2 groups is such that all intramolecular inter-CO_2 group O···O contacts are greater than 3.0 Å, indicating the absence of any intramolecular hydrogen bonding. The large dihedral angles also indicate that in this solid phase there is very little resonance stabilization of carboxyl or carboxylate groups with the benzene ring.

Since the analysis of the X-ray data did not yield the positions of hydrogen atoms, the location of the two protons of the mellitate acid anion could not be definitely determined. However, a consideration of C–O bond distances and the presumed location of hydrogen bonds do allow tentative placement of the acid protons on carboxyl oxygen atoms O(9) and O(6). This follows from the long C–O bond lengths of 1.336 Å (C(11)–O(9)) and 1.301 Å (C(8)–O(6)) and also from the fact that these two oxygen atoms are involved in strong intermolecular hydrogen bonds (O(9)···O(1) = 2.530 Å; O(6)···O(12) = 2.465 Å). The possibility that these extremely short O···O separations are indicative of symmetrical hydrogen bonds cannot be excluded.[13] Although the C–O distances related to the longer O(9)···O(1) hydrogen bond are significantly different (C(11)–O(9) = 1.336 Å vs. C(7)–O(1) = 1.284 Å), implying a nonsymmetrical hydrogen bond with the hydrogen atom more closely associated with O(9), the C–O distances of the shorter O(6)···O(12) hydrogen bond are not significantly different (C(9)–O(6) = 1.301 Å vs. C(12)–O(12) = 1.291 Å), implying a more equally shared hydrogen atom, i.e., a more symmetrical hydrogen bond. If the assignment of acid hydrogen atom positions given above is correct, then the two un-ionized carboxyl groups are related meta to each other, consistent with the Purdie, Tomson, and Riemann[4] suggestion of a symmetrical order of ionization which they deduced from an interpretation of the thermodynamics of mellitic acid ionization. It is of interest to note, as mentioned above, that these carboxyl groups are significantly twisted (dihedral angles of 57 and 47°) from the plane of the benzene ring.

The two independent calcium ions are coordinated to meta-related carboxylate groups and have very similar environments in the Ca_2H_2mellitate structure (Figure 4); in comparison with the structures of other calcium complexes,[14] these environments are not unusual. Ca(1) contains seven oxygen atoms in the primary coordination sphere and Ca(2) eight with typical Ca–O distances (Table II). Assuming for descriptive purposes that the bidentate carboxylate occupies one site, we can describe the coordination polyhedra about the two calcium ions as follows: for Ca(1), a distorted octahedron with the bidentate carboxylate group and three water molecules in equatorial positions and symmetry-related monodentate car-

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boxylates in the two axial positions; for Ca(2), a distorted pentagonal bipyramid with the bidentate carboxylate and four water molecules in equatorial positions and symmetry-related monodentate carboxylates axially disposed. The primary mode of bonding to the mellitate ring involves a four-membered chelate ring containing the calcium ion and both oxygen atoms of the carboxylate group. This mode of bonding is commonly found for calcium ion coordination to organic carboxylates; for example, it has previously been observed as the primary mode of calcium ion binding in calcium malate dihydrate,[15] calcium fumarate trihydrate,[16] and calcium terephthalate trihydrate.[5] The interaction of Ca^{2+} with a benzenepolycarboxylate containing ortho-related carboxylates (e.g., mellitate with two or less acid hydrogens[17]) might conceivably involve the formation of a seven-membered chelate ring containing Ca^{2+} and the two ortho-related carboxylates; this would require the rotation of the two carboxylates to suitable positions with a minimum of steric strain. Models can be constructed which indicate that the two carboxylates can be suitably placed without any restrictive steric interactions. However, evidence of such binding was not found in the structure of the Ca_2H_2mellitate crystal. We therefore prefer to believe that the four-membered ring formation involving the Ca^{2+} and a single carboxylate provides the most stable metal-ligand interaction in such a complex. The presence of seven-membered ring formation, of course, cannot be ruled out in aqueous solution and may well be involved as a (transition) state of binding in the rapidly exchanging Ca^{2+}-ligand solution system.

To the best of our knowledge, only one other Ca^{2+}-benzenecarboxylate (1:1) binding constant has been reported:[18] Ca^{2+}phthalate^{2-}, log K_{11} = 1.07 (IS = 0.15). The significantly larger value of log K_{11} = 3.05 (IS = 0.10) for Ca^{2+}mellitate^{6-} is not unexpected due to the higher charge of the anion and the presence of six carboxylates which are all equally available for binding with Ca^{2+} in the course of the rapid exchange processes occurring in aqueous solution. Perhaps an even stronger interaction might be expected between Ca^{2+} and a highly charged ligand such as mellitate^{6-} (pK_6 = 7.49). However, this charge is evenly distributed over a relatively large, probably highly hydrated molecule; and, apparent from the structural analysis of Ca_2H_2mellitate, the effectiveness of this charge with respect to binding Ca^{2+} cannot be augmented by suitable chelation as, for example, in the calcium complex of EDTA^{4-}[19] which has a stability constant of log K = 10.6.[20] It is of interest to compare the stability of the Ca^{2+}mellitate binding with that of Ca^{2+}oxydiacetate^{2-} which has a very similar 1:1 stability constant (log K = 3.4).[21] Relative to mellitate, the ODA anion is of considerably lower charge and contains fewer binding sites; however the stability of the CaODA complex is derived to a large degree from the ability to form two fused five-membered chelate rings involving both carboxylates and the ether oxygen atom.[14] In view of the characteristics of the mellitate anion (e.g., high charge and multiple, separated binding sites), in solutions of relatively high Ca^{2+} concentration the presence of complexes with more than one Ca^{2+} per ligand is also to be expected. In fact, in order to suitably fit the calcium electrode titration data it was necessary to assume, in addition to the 1:1 complex, the presence of a complex of stoichiometry Ca_2(mellitate)$^{2-}$ with a stability constant (K_{21} = 0.37 × 10^3) of a magnitude not greatly different from the 1:1 complex.

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Registry No. Ca_2H_2mellitate·$9H_2O$, 64189-25-9.

Supplementary Material Available: Listings of anisotropic thermal parameters (Table A-1), structure factor amplitudes (Table A-II), [Ca^{2+}] vs. emf standard curve (Figure A-1), and titration data containing [Ca^{2+}] and the average number of Ca^{2+} ions bound per ligand (Table A-III) (16 pages). Ordering information is given on any current masthead page.

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Bis(dithiocarbamato)-Nitrosyl Complexes of Ruthenium

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The synthesis of new dithiocarbamato complexes of ruthenium is reported including *trans*-[RuNO(S_2CNRR′)$_2$Cl] (R = R′ = Me, Et; R = Me, R′ = Et; R = Me, R′ = Ph), *trans*-[RuNO(S_2CNMe$_2$)$_2$OH]·CH_3OH, *trans*-[RuNO(S_2CNMe$_2$)$_2$$H_2O$]$BF_4$, *trans*-[RuNO($S_2$CNMe$_2$)$_2$$CH_3OH$]$PF_6$, *cis*-[RuNO($S_2$CNMe$_2$)$_2$X] (X = F, Br, I, NO_2), *cis*-[RuNO(S_2CNRR′)$_2$X] (X = Br, I; R = R′ = Et; R = Me, R′ = Et), and *cis*- and *trans*-[RuNO(S_2CNMe$_2$)$_2$X] (X = N_3, SCN, NCO). In contrast with the iron complex, *cis*-Ru(NO)($^{15}NO_2$)(S_2CNMe$_2$)$_2$ does not undergo exchange between the NO and NO_2 ligands. The spectral characteristics of these complexes are discussed in relation to their geometric configuration. The ^{13}C NMR spectra of many of these complexes are reported and give valuable information regarding the bound ligand. The rotation of the unidentate dithiocarbamate ligand in *cis*-[RuNO(S_2CNMe$_2$)$_3$] is clearly differentiated from the two bidentate ligands.

Introduction

Sulfur ligands stabilize numerous nitrosyl complexes, but few sulfur derivatives of ruthenium nitrosyls have been reported. Those ruthenium complexes which are known include *cis*-Ru(NO)(S_2CNR_2)$_3$ (R = Me, Et),[1,2] *trans*-Ru(NO)(Cl)(SacSac)$_2$,[3] RuX_3(NO)L_2 (X = Cl, Br; L = Me_2S, Et_2S, PhEtS, PhMeS, (n-Pr)$_2$S, n-PrPhS),[4] and [RuBr_3(NO)-

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