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References

- CRUICKSHANK, D. W. J. (1965). *Computing Methods in Crystallography*, edited by J. S. ROLLETT, pp. 112–116. Oxford: Pergamon Press.
- GERMAIN, G., MAIN, P. & WOOLFSON, M. M. (1971). *Acta Cryst.* **A27**, 368–376.
- GIRLING, R. L. & AMMA, E. L. (1968). *Chem. Commun.* pp. 1487–1488.
- GIRLING, R. L. & AMMA, E. L. (1971). *Inorg. Chem.* **10**, 335–340.
- HUNT, G. W., GRIFFITH, E. A. H. & AMMA, E. L. (1976). *Inorg. Chem.* **15**, 2993–2997.
- IMMIRZI, A. (1967). *Ric. Sci.* **37**, 743–749.
- IMMIRZI, A. (1976). *Acta Cryst.* **A33**, 216–218.
- International Tables for X-ray Crystallography* (1974). Vol. IV, pp. 99, 149. Birmingham: Kynoch Press.
- JOHNSON, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.
- KOWAL, A. & KEDZIA, B. B. (1976). *Bull. Acad. Pol. Sci. Sér. Sci. Chim.* **24**, 549–557.
- LUTH, H., HALL, E. A., SPOFFORD, W. A. & AMMA, E. L. (1969). *Chem. Commun.* pp. 520–521.
- PAULING, L. (1960). *The Nature of the Chemical Bond*, p. 246. Ithaca: Cornell Univ. Press.
- PIGNEDOLI, A. & PEYRONEL, G. (1976). *Spectrochim. Acta Part A*, **32**, 1739–1741.
- PIGNEDOLI, A. & PEYRONEL, G. (1977). *Acta Cryst.* **B33**, 1439–1443.
- PIGNEDOLI, A., PEYRONEL, G. & ANTOLINI, L. (1972). *Gazz. Chim. Ital.* **102**, 679–686.
- PIGNEDOLI, A., PEYRONEL, G. & ANTOLINI, L. (1973). *Acta Cryst.* **B29**, 1490–1499.
- SPOFFORD, W. A. III & AMMA, E. L. (1970). *Acta Cryst.* **B26**, 1474–1483.
- SPOFFORD, W. A. III & AMMA, E. L. (1972). *J. Cryst. Mol. Struct.* **2**, 151–158.

Acta Cryst. (1979). **B35**, 2013–2020

Schiff-Base Complexes of Calcium: Crystal Structure Analysis of Dinitrato[*N,N'*-propane-1,3-diylbis(salicylideneimine)]calcium(II) and the Spectroscopic Properties of Some Related Complexes

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Abstract

The title compound, $[\text{Ca}(\text{C}_{17}\text{H}_{18}\text{N}_2\text{O}_2)(\text{NO}_3)_2]$, $\text{C}_{17}\text{H}_{18}\text{CaN}_4\text{O}_8$, is orthorhombic with $a = 37.166$ (3), $b = 10.181$ (1), $c = 5.111$ (0) Å, $Z = 4$, space group $P2_12_12_1$. The structure was refined to $R = 0.026$ for 1511 counter reflections. The Schiff base is present in a hitherto unreported charge-separated form with the ligand bridging two Ca ions through negatively charged O atoms. The azomethine N atoms are not coordinated; they carry the protons which are transferred from the phenolic groups on complex formation and form intramolecular hydrogen bonds with the O atoms. A bidentate, chelating nitrate ion is coordinated to each Ca ion while a pair of equivalent, bridging nitrate ions complete eight-coordination about Ca^{II} by the formation of chelate rings to the separate Ca ions. The stereochemistry around Ca is best described as a distorted hexagonal bipyramid. Nine Schiff-base complexes have been prepared with *N,N'*-propane-1,3-diylbis(salicylideneimine) and related bases, H_2L , with

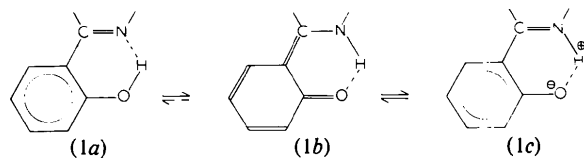
the stoichiometries $\text{Ca}(\text{H}_2\text{L})\text{X}_2 \cdot n\text{EtOH}$ [$\text{X} = (\text{NO}_3)^-$ or Cl^- , $n = 0$ or 2] and $\text{Ca}(\text{H}_2\text{L})_2\text{X}_2 \cdot n\text{S}$ [$\text{X} = (\text{NO}_3)^-$ or Cl^- , $n = 0$ or 1, $\text{S} = \text{EtOH}$ or H_2O]. Since the infrared spectra of the coordinated Schiff bases are so similar, it is concluded that the complexes are closely related structurally. The mode of coordination of Schiff bases in a large number of similar compounds of other metal ions is discussed.

Introduction

Schiff bases containing phenolic groups, such as *N,N'*-ethylenebis(salicylideneimine), H_2salen , form metal-ion complexes in two ways. In the first (and better understood), the ligand is ionized by the removal of the acidic protons attached to O, giving complexes such as $\text{Cu}(\text{salen})$. In the second, the base is apparently either un-ionized or partly ionized. In this case, the metal ion usually has class A character [$\text{La}^{\text{III}} - \text{Lu}^{\text{III}}$ (except Pm); $M^{\text{IV}} = \text{Ti, Nb, Th, U, Sn, Zr, Hf; Fe}^{\text{III}}; \text{Co}^{\text{II}}$;

UO₂²⁺] and typical examples are TiCl₄(H₂salen), LaCl₃(H₂salen)₂, SnCl₄(HL)₂ (HL = *N*-salicylideneaniline), and LaCl(HL)₂(OH₂) (H₂L = *N*-salicylideneanthranilic acid). In the last case, the carboxylate protons are ionized on complex formation. Although many examples (Bullock & Tajmir-Riahi, 1977, and references therein) of the second type are known, none has been the subject of crystallographic study, unlike the more numerous examples of the first type where a great variety of studies have been conducted.

In limited studies of complexes of the second type Bullock & Tajmir-Riahi (1977) and others concluded from infrared spectra evidence that only the azomethine N atoms are coordinated with the ligand present in the enol-amine form (1a) while other workers predicted, from essentially identical infrared results and further evidence from ultraviolet spectroscopy (Condorelli, Fragala, Guiffrida & Cassol, 1975), that the keto-enamine tautomer (1b) is more important and that the O atoms only are coordinated in the complexes. During some work with the trivalent lanthanoids, we found that Ca^{II} forms the same type of complexes (ionic radii: Ca^{II} 1.06, La^{III} 1.04 Å). The crystallographic study reported here reveals that the previously unconsidered, charge-separated tautomer, (1c), predominates in the complexes.



In addition to the title compound, H₂salpd forms Ca(H₂salpd)₂(NO₃)₂·H₂O and CaCl₂(H₂salpd)₂·2H₂O; H₂salen forms Ca(H₂salen)₂(NO₃)₂ and CaCl₂(H₂salen)₂·2EtOH; *N,N'*-propylenebis(salicylideneimine), H₂salpn, forms Ca(H₂salpn)₂(NO₃)₂·EtOH and CaCl₂(H₂salpn)₂·H₂O; and *N,N'*-hexane-1,6-diylbis(salicylideneimine), H₂salhxn, forms Ca(H₂salhxn)₂(NO₃)₂ and CaCl₂(H₂salhxn)₂. From

their infrared spectra these compounds are closely related structurally to Ca(H₂salpd)(NO₃)₂.

Experimental

None of the complexes has been described previously. They were prepared by the addition of the appropriate hydrated Ca salt [CaCl₂·2H₂O or Ca(NO₃)₂·4H₂O] in absolute ethanol to a hot solution of the ligand in absolute ethanol. A yellow precipitate formed almost immediately. This was filtered off, washed with cold ethanol several times, and dried (CaCl₂). Standard analytical procedures were used and the results are given in Table 1. Infrared spectra were recorded routinely.

Crystals of Ca(H₂salpd)(NO₃)₂ were obtained from aqueous ethanol as pale yellow prisms, elongated parallel to *c*. The crystals develop the forms {001}, {520}, and {100}, in decreasing order of prominence. Unit-cell and space-group data were obtained from Weissenberg photographs, and accurate cell dimensions by a weighted ($w = \tan \theta$) least-squares fit to the θ values of 20 high-order reflections measured on a Siemens diffractometer (AED) with Ni-filtered Cu *K* α radiation ($\lambda = 1.5418$ Å).

Crystal data

C₁₇H₁₈CaN₄O₈, $M_r = 446.41$, orthorhombic, $a = 37.166$ (3), $b = 10.181$ (1), $c = 5.111$ (0) Å, $V_c = 1934.0$ (4) Å³, $D_x = 1.533$ Mg m⁻³, $Z = 4$, $F(000) = 928$, $\mu(\text{Cu } K\alpha) = 3.29$ mm⁻¹, space group $P2_12_12_1$.

A crystal 0.15 × 0.10 × 0.30 mm, parallel to *a*, *b* and *c* respectively, was selected for intensity measurements. The intensities of 1644 symmetry-independent reflections with $\lambda^{-1} \sin \theta \leq 0.57$ Å⁻¹ were measured on the diffractometer with the five-value technique (Hoppe, 1965). A reference reflection, monitored every 20 reflections, showed that there was no crystal decomposition. The data were scaled, first in blocks of

Table 1. Summary of infrared results (H₂salen, 1635, 1285; H₂salpn, 1632, 1280; H₂salpd, 1633, 1280; H₂salhxn, 1630, 1280) (cm⁻¹) and analytical data (%)

Complex	C=N stretch	C-O stretch	Found							Calculated			
			Ca	C	H	N	Cl	Ca	C	H	N	Cl	
(i) Ca(H ₂ salpd)(NO ₃) ₂	1645	*	8.8	46.0	4.1	12.9	—	9.0	45.7	4.1	12.6	—	
(ii) Ca(H ₂ salpd) ₂ (NO ₃) ₂ ·H ₂ O	1642	1282	5.3	54.1	4.9	11.1	—	5.4	54.7	5.1	11.3	—	
(iii) Ca(H ₂ salen) ₂ (NO ₃) ₂	1640	1280	5.6	54.5	4.6	10.2	—	5.7	54.8	4.6	10.1	—	
(iv) Ca(H ₂ salpn) ₂ (NO ₃) ₂ ·EtOH	1630	1280	5.1	55.4	5.4	10.9	—	5.2	55.8	5.5	10.8	—	
(v) Ca(H ₂ salhxn) ₂ (NO ₃) ₂	1640	1290	4.9	58.9	5.9	10.2	—	4.9	59.1	6.0	10.3	—	
(vi) CaCl ₂ (H ₂ salen) ₂ ·2EtOH	1640	1282	8.5	51.2	5.9	6.1	15.1	8.5	51.0	6.0	5.9	15.0	
(vii) CaCl ₂ (H ₂ salpn) ₂ ·H ₂ O	1645	1282	9.5	59.2	5.7	7.8	10.1	5.8	58.9	5.5	8.1	10.2	
(viii) CaCl ₂ (H ₂ salpd) ₂ ·2H ₂ O	1640	1290	5.5	48.2	4.9	6.3	16.8	9.3	47.6	5.2	6.5	16.5	
(ix) CaCl ₂ (H ₂ salhxn) ₂	1640	1285	5.1	62.8	6.5	7.1	9.2	5.3	63.2	6.4	7.4	9.3	

* Vibration covered by strong nitrate-ion vibration (see discussion).

twenty between pairs of reference reflections, and then to a common value.

The intensities were corrected for Lorentz, polarization, and absorption effects, the latter by a Gaussian integration technique over a grid of 1400 points. Each measured intensity was assigned a variance based on counting statistics, and 1511 reflections for which $I \geq 2.58\sigma(I)$ were used in the structure analysis. The average value of $\sigma(|F_o|)/|F_o|$ was 0.017 for these reflections and 0.023 overall.

Structure determination and refinement

The Ca atom was located from a sharpened Patterson map, and used to provide partial phase information for a direct-methods solution of the structure. This procedure was successful in that the resulting E map with the highest figure of merit resolved the Ca and 15 other atoms. Fourier techniques located the remaining non-hydrogen atoms, and isotropic least squares refined the structure from $R = 0.22$ to $R = 0.11$. To complete the analysis, anisotropic refinement was used for the non-hydrogen atoms; all H atoms were located from a difference synthesis and refined isotropically and a weighting scheme ($\{w = 1 + [(|F_o| - B)/A]^2\}^{-1}$, with $A = 60$ and $B = 7.5$) was introduced. The refinement converged at $R = 0.026$.* Analysis of the $w\Delta^2$ values in ranges of $|F_o|$ showed that the weighting scheme was satisfactory. The final difference map showed a zero field except for a very small region of $0.2 \text{ e } \text{Å}^{-3}$ near

* Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34422 (19 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

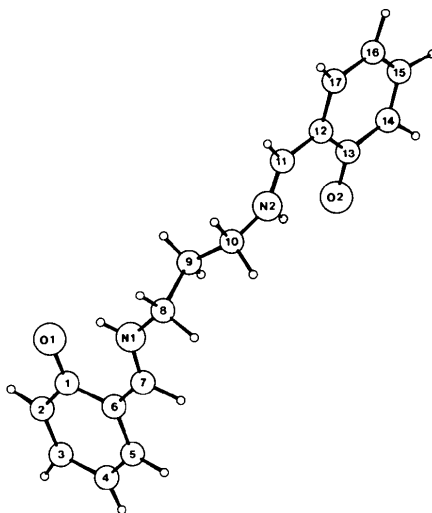


Fig. 1. Stereochemistry of coordinated H_2salpd , and numbering scheme.

the position of the Ca atom. At convergence the final shifts were 0.05 times the corresponding e.s.d.'s.

Results and discussion

Description of the structure of $\text{Ca}(\text{H}_2\text{salpd})(\text{NO}_3)_2$

The atomic parameters are listed in Table 2, bond lengths and angles in Tables 3 and 4. Fig. 1 shows the stereochemistry and the numbering scheme for coordinated H_2salpd , Fig. 2 the coordination around Ca and the numbering scheme for the nitrate ions, and Fig.

Table 2. Atomic coordinates

	x	y	z
Ca	0.37439 (2)	0.81036 (6)	0.7048 (1)
O(1)	0.41643 (6)	0.9689 (2)	0.7121 (6)
O(2)	0.32164 (5)	0.6911 (2)	0.7535 (4)
O(3)	0.43163 (7)	0.4662 (2)	0.6713 (6)
O(4)	0.39700 (7)	0.6004 (3)	0.8849 (6)
O(5)	0.41813 (8)	0.6570 (3)	0.5172 (6)
O(6)	0.34357 (7)	0.9839 (3)	-0.0037 (5)
O(7)	0.36866 (6)	0.8245 (2)	0.2081 (5)
O(8)	0.34095 (7)	0.9770 (3)	0.4212 (5)
N(1)	0.41611 (7)	0.1720 (3)	0.0217 (6)
N(2)	0.32781 (7)	0.5189 (3)	1.1324 (6)
N(3)	0.41614 (7)	0.5725 (3)	0.6903 (7)
N(4)	0.35053 (7)	0.9305 (3)	0.2083 (7)
C(1)	0.44679 (9)	0.0115 (3)	0.6155 (8)
C(2)	0.46432 (10)	-0.0533 (4)	0.4071 (8)
C(3)	0.49595 (10)	-0.0061 (4)	0.3076 (9)
C(4)	0.51218 (10)	0.1073 (4)	0.4068 (9)
C(5)	0.49598 (10)	0.1729 (4)	0.6067 (8)
C(6)	0.46315 (8)	0.1278 (3)	0.7147 (8)
C(7)	0.44682 (9)	0.2015 (3)	0.9167 (8)
C(8)	0.39792 (10)	0.2531 (4)	1.2182 (8)
C(9)	0.36508 (9)	0.3203 (3)	1.0973 (8)
C(10)	0.35116 (9)	0.4285 (3)	1.2768 (8)
C(11)	0.29602 (9)	0.5574 (3)	1.2067 (8)
C(12)	0.27593 (8)	0.6548 (3)	1.0715 (8)
C(13)	0.29018 (8)	0.7214 (3)	0.8511 (7)
C(14)	0.26882 (9)	0.8229 (4)	0.7407 (9)
C(15)	0.23561 (10)	0.8534 (4)	0.8410 (9)
C(16)	0.22205 (10)	0.7879 (4)	1.0614 (9)
C(17)	0.24164 (9)	0.6896 (4)	1.1732 (9)
H(2)	0.4536	-0.1301	0.3547
H(3)	0.5089	-0.0559	0.1560
H(4)	0.5335	0.1358	0.3248
H(5)	0.5074	0.2509	0.6834
H(7)	0.4586	0.2864	0.9791
H(81)	0.4166	0.3270	1.2855
H(82)	0.3899	0.1932	1.3639
H(91)	0.3726	0.3602	0.9267
H(92)	0.3448	0.2550	1.0471
H(101)	0.3738	0.4824	1.3594
H(102)	0.3373	0.3842	1.4416
H(11)	0.2851	0.5166	1.3814
H(14)	0.2775	0.8710	0.5745
H(15)	0.2214	0.9299	0.7354
H(16)	0.1986	0.8163	1.1204
H(17)	0.2333	0.6459	1.3258
H(20)	0.4067	0.0865	0.9605
H(21)	0.3350	0.5531	0.9763

Table 3. *Bond lengths* (Å)

C(1)–C(2)	1.412 (5)	C(2)–H(2)	0.92 (5)
C(2)–C(3)	1.368 (5)	C(3)–H(3)	1.04 (5)
C(3)–C(4)	1.397 (6)	C(4)–H(4)	0.94 (5)
C(4)–C(5)	1.361 (6)	C(5)–H(5)	0.98 (5)
C(5)–C(6)	1.416 (5)	C(7)–H(7)	1.02 (5)
C(6)–C(1)	1.424 (5)	C(8)–H(81)	1.08 (4)
C(6)–C(7)	1.413 (5)	C(8)–H(82)	1.01 (5)
C(1)–O(1)	1.306 (4)	C(9)–H(91)	1.00 (5)
C(7)–N(1)	1.297 (5)	C(9)–H(92)	1.04 (5)
N(1)–C(8)	1.466 (5)	C(10)–H(101)	1.09 (4)
C(8)–C(9)	1.530 (5)	C(10)–H(102)	1.09 (5)
C(9)–C(10)	1.524 (5)	C(11)–H(11)	1.07 (5)
C(10)–N(2)	1.465 (5)	C(14)–H(14)	1.03 (6)
N(2)–C(11)	1.301 (4)	C(15)–H(15)	1.08 (5)
C(11)–C(12)	1.420 (5)	C(16)–H(16)	0.97 (5)
C(12)–C(13)	1.418 (5)	C(17)–H(17)	0.95 (6)
C(13)–C(14)	1.420 (5)	N(1)–H(20)	0.99 (5)
C(14)–C(15)	1.372 (5)	N(2)–H(21)	0.91 (5)
C(15)–C(16)	1.403 (6)	O(1)–H(20)	1.78 (5)
C(16)–C(17)	1.363 (6)	O(2)–H(21)	1.88 (5)
C(17)–C(12)	1.421 (5)	O(1)–N(1) ⁱⁱ	2.603 (4)
C(13)–O(2)	1.308 (4)	O(2)–N(2)	2.622 (4)
N(3)–O(3)	1.230 (4)	Ca–O(1)	2.247 (2)
N(3)–O(4)	1.255 (4)	Ca–O(2)	2.319 (2)
N(3)–O(5)	1.236 (4)	Ca–O(4)	2.474 (3)
N(4)–O(6)	1.240 (4)	Ca–O(5)	2.450 (3)
N(4)–O(7)	1.272 (4)	Ca–O(7) ⁱ	2.585 (3)
N(4)–O(8)	1.239 (4)	Ca–O(6) ⁱ	2.579 (3)
		Ca–O(8)	2.554 (3)
		Ca–O(7)	2.552 (3)

There is no short Ca link to O(3): Ca...O(3) 4.10 Å, \angle Ca–O(3)–N(3) 5.1°. The nearest neighbour of O(3) is H(7) at 2.61 Å.

Symmetry code: (i) $x, y, 1 + z$; (ii) $x, 1 + y, 1 + z$.

Table 4. *Bond angles* (°)

C(6)–C(1)–C(2)	117.4 (3)	C(1)–O(1)–H(20)	103 (2)
C(1)–C(2)–C(3)	120.8 (4)	O(1)–H(20)–N(1)	138 (4)
C(2)–C(3)–C(4)	121.7 (4)	H(20)–N(1)–C(7)	113 (3)
C(3)–C(4)–C(5)	119.1 (4)	H(20)–N(1)–C(8)	123 (3)
C(4)–C(5)–C(6)	121.0 (4)	C(13)–O(2)–H(21)	100 (1)
C(5)–C(6)–C(1)	119.9 (3)	O(2)–H(21)–N(2)	138 (4)
C(2)–C(1)–O(1)	121.9 (3)	H(21)–N(2)–C(11)	114 (3)
C(6)–C(1)–O(1)	120.7 (3)	H(21)–N(2)–C(10)	120 (3)
C(1)–C(6)–C(7)	121.2 (3)	O(3)–N(3)–O(4)	121.8 (3)
C(5)–C(6)–C(7)	118.9 (3)	O(4)–N(3)–O(5)	116.3 (3)
C(6)–C(7)–N(1)	123.9 (3)	O(5)–N(3)–O(3)	121.9 (3)
N(1)–C(8)–C(9)	110.1 (3)	O(6)–N(4)–O(7)	118.8 (3)
C(8)–C(9)–C(10)	110.5 (3)	O(7)–N(4)–O(8)	118.5 (3)
C(9)–C(10)–N(2)	110.6 (3)	O(8)–N(4)–O(6)	122.7 (3)
N(2)–C(11)–C(12)	123.1 (3)	O(1)–Ca–O(2)	164.17 (9)
C(12)–C(13)–C(14)	117.1 (3)	O(1)–Ca–O(4)	112.23 (9)
C(13)–C(14)–C(15)	121.2 (4)	O(1)–Ca–O(5)	90.16 (9)
C(14)–C(15)–C(16)	121.1 (4)	O(2)–Ca–O(4)	78.18 (8)
C(15)–C(16)–C(17)	119.6 (4)	O(2)–Ca–O(5)	105.63 (9)
C(16)–C(17)–C(12)	120.6 (4)	O(4)–Ca–O(5)	50.91 (10)
C(17)–C(12)–C(13)	120.4 (3)	O(1)–Ca–O(6)	78.87 (8)
C(14)–C(13)–O(2)	121.3 (3)	O(1)–Ca–O(7)	91.93 (9)
C(12)–C(13)–O(2)	121.6 (3)	O(1)–Ca–O(7')	90.04 (9)
C(13)–C(12)–C(11)	121.6 (3)	O(1)–Ca–O(8)	82.53 (8)
C(17)–C(12)–C(11)	117.9 (3)	O(5)–Ca–O(7)	72.61 (8)
C(7)–N(1)–C(8)	124.0 (3)	O(7)–Ca–O(8)	50.01 (7)
C(10)–N(2)–C(11)	125.5 (3)	O(8)–Ca–O(6)	69.95 (8)
		O(6)–Ca–O(7')	49.52 (6)
		O(7')–Ca–O(4)	72.89 (8)

3 a packing diagram as seen along [001]. Fig. 3 shows that all Ca ions and all H₂salpd molecules are stereochemically equivalent while Fig. 2 illustrates the eight-coordination around Ca.

The stereochemistry about Ca is best described as a distorted hexagonal bipyramid with the hexagon plane containing nitrate-ion O atoms only and the polyhedron completed by the phenolic O(1) and O(2). The angle O(1)–Ca–O(2) is 164.2° and the plane formed by these atoms forms an angle of 83.5° with the hexagon plane (plane 9). The main distortions in the hexagon plane are caused by [N(3)O₃][–] for which the coordinated O(4) and O(5) are above and below the plane. The bite of the nitrate ion constrains the angles subtended at Ca such that the three angles involving coordinated nitrate are smaller (by about 20°) than the other three (Table 5).

Each molecule of H₂salpd bridges a pair of Ca ions with each negatively charged O atom [O(1)···H(20) 1.78 (5), O(2)···H(21) 1.88 (5) Å] bonded to a single metal ion. The azomethine N atoms are not coordinated and carry protons transferred from O atoms on coordination of the ligand (see below). Intramolecular hydrogen bonds connect these H atoms and the phenolic O atoms. The phenyl rings are essentially planar (planes 3 and 4, Table 5) but there is a large angle between the planes (75.5°) within each H₂salpd molecule. This arises in the main from a rotation about C(11)–C(12) with respect to C(6)–C(7) and the rest of

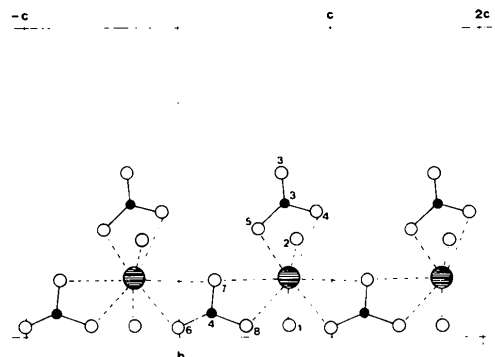


Fig. 2. Stereochemistry about the calcium ion, and numbering scheme for the nitrate ion.

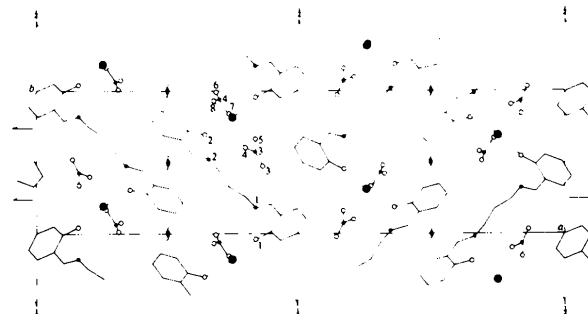


Fig. 3. Packing diagram of Ca(H₂salpd)(NO₃)₂ viewed along [001].

the molecule. A similar angle (56.8°) was found for N,N' -(*o*-phenylene)bis(salicylideneimine), $H_2salphen$, the only free base of this type for which accurate structural data are available (Pahor, Calligaris, Delise, Dodic, Nardin & Randaccio, 1976). This was said to be caused by the intramolecular hydrogen-bonding schemes in the two salicylideneimine residues which, in a coplanar configuration, would give rise to steric hindrance between the H atoms corresponding to H(20) and H(21) in our scheme. However, in

$Ca(H_2salpd)(NO_3)_2$, H(20) and H(21) are well separated and a fully conjugated system could not be formed even if the two rings were rigorously coplanar since the C(8)–C(9) and C(9)–C(10) lengths were close to those expected for sp^3 hybridization at C(8), C(9) and C(10). Also, the ring C(1)–C(6) is not coplanar with the C(6), C(7), H(7) plane (2.5°) but there are only small angles between planes 7 and 8, 5 and 6, 3 and 6, and 4 and 8 which confirms the sp^2 hybridization for N(1), N(2), C(7), and C(11).

Table 5. Equations of least-squares planes (x , y and z are fractional atomic coordinates) with their *r.m.s.* errors of fit, deviations (Å) of atoms from planes with their *e.s.d.*'s in parentheses, and dihedral angles ($^\circ$) with their *e.s.d.*'s in parentheses

Least-squares planes

Plane 1: N(3), O(3), O(4), O(5)

$$29.758x + 3.980y + 2.320z = 16.258; 0.003$$

N(3)	0.004 (2)	C(7)	-0.033 (3)
O(3)	-0.002 (2)	Ca	-0.256 (1)
O(4)	-0.001 (3)		
O(5)	-0.001 (3)		

Plane 2: N(4), O(6), O(7), O(8)

$$31.569x + 5.344y + 0.280z = 16.102; 0.004$$

N(4)	-0.006 (2)	C(11)	-3.44 (3)
O(6)	0.002 (3)	Ca	0.245 (1)
O(7)	0.002 (2)		
O(8)	0.002 (3)		

Plane 3: C(1)–C(6)

$$18.962x - 5.619y + 3.371z = 10.478; 0.003$$

C(1)	0.005 (3)	O(1)	-0.006 (3)
C(2)	-0.001 (3)	H(2)	0.050 (30)
C(3)	-0.002 (3)	H(3)	0.012 (30)
C(4)	0.003 (3)	H(4)	-0.030 (30)
C(5)	0.001 (3)	H(5)	0.037 (30)
C(6)	-0.004 (3)	H(7)	-0.091 (30)
C(7)	-0.047 (3)	H(81)	-0.082 (30)
N(1)	-0.110 (3)	H(20)	-0.013 (30)

Plane 4: C(12)–C(17)

$$16.063x + 6.810y + 3.091z = 12.206; 0.006$$

C(12)	-0.002 (3)	N(2)	0.094 (3)
C(13)	-0.000 (3)	C(11)	0.076 (3)
C(14)	0.006 (3)	H(11)	0.162 (30)
C(15)	-0.010 (4)	H(14)	-0.041 (30)
C(16)	0.007 (4)	H(15)	-0.042 (30)
C(17)	-0.001 (4)	H(16)	0.007 (30)
O(2)	-0.003 (3)	H(17)	0.039 (30)
O(3)	-0.022 (2)	H(21)	-0.040 (30)
O(6)	0.002 (3)	H(102)	0.285 (30)
O(7)	-0.026 (2)		

Dihedral angles

Planes	Planes	Planes	Planes	Planes	Planes	Planes	
1, 2	24.5 (4)						
1, 3	60.5 (4)	2, 3	79.2 (4)				
1, 4	28.1 (5)	2, 4	41.3 (5)	3, 4	75.5 (5)		
1, 5	58.3 (3)	2, 5	77.9 (3)	3, 5	2.5 (3)	4, 5	73.0 (4)
1, 6	56.3 (3)	2, 6	76.8 (3)	3, 6	6.3 (3)	4, 6	69.6 (3)
1, 7	28.0 (3)	2, 7	38.2 (3)	3, 7	79.0 (3)	4, 7	4.8 (3)
1, 8	31.5 (3)	2, 8	38.2 (3)	3, 8	84.3 (3)	4, 8	9.5 (3)
						5, 6	3.9 (0)
						5, 7	76.5 (0)
						6, 7	73.3 (0)
						5, 8	81.8 (0)
						6, 8	78.6 (0)
						7, 8	5.3 (0)

Plane 5: C(6), C(7), H(7)

$$19.382x - 5.241y + 3.478z = 10.792; \text{zero}$$

C(1)	-0.052 (3)	C(5)	0.024 (3)
C(2)	-0.098 (3)	O(1)	-0.081 (3)
C(3)	-0.078 (3)	N(1)	-0.075 (3)
C(4)	-0.013 (3)		

Plane 6: C(8), N(1), H(20)

$$18.939x - 4.725y + 3.703z = 10.851; \text{zero}$$

C(1)	-0.165 (3)	C(6)	-0.037 (3)
C(5)	-0.029 (3)	C(7)	0.053 (3)

Plane 7: C(11), C(12), H(11)

$$16.733x + 7.263y + 2.744z = 12.314; \text{zero}$$

C(13)	0.118 (3)	C(17)	-0.042 (4)
C(14)	0.195 (3)	O(2)	0.156 (3)
C(15)	0.135 (4)	N(2)	0.048 (3)
C(16)	0.037 (4)		

Plane 8: C(10), N(2), H(21)

$$15.460x + 7.883y + 2.438z = 11.919; \text{zero}$$

C(11)	-0.007 (3)	C(13)	0.329 (3)
C(12)	0.120 (3)	C(14)	0.113 (3)

Plane 9: Ca, O(4), O(5), O(6), O(7), O(7'), O(8)

$$30.740x + 5.708y + 0.202z = 16.241; 0.277$$

Ca	0.037 (1)	O(7)	-0.159 (2)
O(4)	-0.431 (3)	O(7')	0.044 (2)
O(5)	0.466 (3)	O(8)	-0.097 (3)
O(6)	0.139 (3)		

The angle between plane 9 and the plane formed by Ca, O(1), O(2) is $83.5 (4)^\circ$.

Comparisons with previously determined structures (Table 6)

Throughout this section the numbering scheme shown in the left-hand side of Fig. 1 will be used: where there are differences in bond lengths and angles for the two halves of any molecule mean values will be given so that, for instance, C(1)–O(1) refers to the mean of C(1)–O(1) and C(13)–O(2) for Ca(H₂salpd)(NO₃)₂.

For H₂salphen (Pahor *et al.*, 1976), the enol–imine tautomer (1*a*) predominates over the keto–enamine form (1*b*) since H(20) and H(21) are located close to the O atoms; C(7)–N(1) is much shorter than C(6)–C(7), and C(1)–O(1) was near to but below a range found for substituted phenols [1.355 (2)–1.377 (4) Å]. However, some contribution from (1*b*) is present since C(1)–C(2), C(1)–C(6), and C(5)–C(6) are longer than any of the other acyl bond lengths with C(3)–C(4) slightly longer than either C(2)–C(3) or C(4)–C(5); also C(7)–N(1) was at the top end of a reported range for –CH=N– [1.262 (4)–1.281 (9) Å]. Bond lengths in the *o*-phenylene ring connecting N(1) and N(2) will not be considered here. On removal of the phenolic protons and formation of a Co^{II} complex of salphen the bond-length differences in the acyl rings persist although C(1)–C(2), C(1)–C(6), and C(5)–C(6) are not much different, with C(7)–C(6) shortening and C(7)–N(1) lengthening on coordination of the O and N atoms. Additionally O(1) and N(1) are moved further apart to accommodate the metal ion. In a series of Fe^{II} and Co^{II} complexes of salen (Calligaris, Nardin & Randaccio, 1971) much the same bond lengths within the coordinated ligand were found.

Table 6. *Comparisons of bond lengths (Å) in a Schiff base and some complexes*

Bond	This work ^(a)	salen complexes ^(b)	H ₂ salphen ^(c)	Co(salphen) ^(d)
C(1)–C(2)	1.416	1.412	1.400	1.429
C(1)–C(6)	1.416	1.416	1.420	1.424
C(5)–C(6)	1.419	1.422	1.406	1.420
C(5)–C(4)	1.362	1.372	1.388	1.380
C(4)–C(3)	1.400	1.395	1.392	1.414
C(3)–C(2)	1.370	1.389	1.384	1.367
C(7)–C(6)	1.422	1.434	1.449	1.412
C(7)–N(1)	1.300	1.291	1.288	1.317
N(1)–C(8)	1.466	1.481	(<i>e</i>)	(<i>e</i>)
C(1)–O(1)	1.306	1.321	1.345	1.299
C(8)–C(9)	1.527	1.510	(<i>e</i>)	(<i>e</i>)
O(1)···N(1)	2.613	(<i>f</i>)	2.600	2.727

(*a*) Means.

(*b*) Means for 17 complexes (Calligaris, Nardin & Randaccio, 1971).

(*c*) Means; the two halves of the molecule are non-equivalent (Pahor *et al.*, 1976).

(*d*) Means of bond lengths for the orthorhombic and monoclinic forms (Pahor *et al.*, 1976).

(*e*) N atoms bonded to *sp*² C atoms.

(*f*) Distances not quoted.

For Ca(H₂salpd)(NO₃)₂ the tautomeric balance is shifted in favour of (1*c*) with a contribution from (1*b*). Here N(1)–H(20) is 0.95 (5) Å and O(1)···H(20) is 1.83 (5) Å with the remainder of the ligand bond lengths similar to those found in Co(salphen) (Pahor *et al.*, 1976) and the salen complexes (Calligaris, Nardin & Randaccio, 1971). As N(1)–C(8) at 1.466 Å is close to the expected bond length of 1.47 Å for N(*sp*²)–C(*sp*³), writing (1*c*) as a major contribution is justified, but the bond lengths within the acyl rings and the shortening of C(1)–O(1) and C(6)–C(7) require a contribution from (1*b*). This would help explain the ultraviolet spectra for some Nd^{III} complexes from which it was deduced that (1*b*) predominates over (1*a*) and ligands of this type were coordinated through ketonic O atoms only; isomer (1*c*) was not considered (Condorelli, Fragala, Guiffrida & Cassol, 1975). Since Ca^{II} is not positioned between O(1) and N(1), the O(1)···N(1) distance is similar to that found in H₂salphen although the proton is on N(1) rather than O(1).

Overall, the effects on the bond lengths of protonating N(1) and coordinating a metal ion to O(1) only in Ca(H₂salpd)(NO₃)₂ are remarkably similar to those caused by the removal of protons by the ionization of the phenolic O atoms and the coordination of a divalent metal ion to all O and N atoms.

Nitrate-ion coordination

As expected the nitrate ions are planar (planes 1 and 2, Table 5), but non-equivalent. One type, [N(3)O₃][–], is bidentate and chelated to a single metal ion in a well established (Addison, Logan, Wallwork & Garner, 1971) asymmetric form. The bond lengths to Ca are not equal and there are three different N(3)–O lengths but the angles O(3)–N(3)–O(4) and O(3)–N(3)–O(5) are equal and greater than O(4)–N(3)–O(5); the nitrate-ion angle constrained by the chelate ring is usually (Addison, Logan, Wallwork & Garner, 1971) the smallest. There are no interactions between O(3) and any other atom except for those within each [N(3)O₃][–] ion; the shortest O(3)···H contact [to H(7)] is 2.61 Å. There is a similar arrangement (Ribár, Divjaković, Herak & Prelesnik, 1973) for the non-bridging nitrate ions in Ca₂(NO₃)₄(OH₂)₈ with, using our numbering scheme, Ca–O(4) 2.562, Ca–O(5) 2.477, N(3)–O(4) 1.251, N(3)–O(5) 1.278 and N(3)–O(3) 1.230 Å. As in our compound O(4)–N(3)–O(5), 115.9°, is smaller than the other two nitrate angles which are almost the same (120.5 and 123.5°).

The other type, [N(4)O₃][–], is bonded in an unusual fashion as O(7) bridges a pair of Ca ions with the plane of the nitrate ion rotated such that chelate rings are completed to each metal ion separately by O(6) and O(8). The bridging atom is asymmetrically placed but not markedly so with Ca–O(7) distances of 2.552 and

2.585 Å, but these and the different bond lengths from O(8) and O(6) to the two Ca ions have very little effect on the bond lengths and angles within the nitrate group since N(4)–O(8) and N(4)–O(6) are equal, as are the angles O(7)–N(4)–O(8) and O(6)–N(4)–O(7). N(4)–O(7) is significantly longer than the other two with the two nitrate angles within the chelate rings smaller than the third. As far as we know there is no analogous structure reported, but the bridging nitrate ion in $\text{Ca}_2(\text{NO}_3)_4(\text{OH}_2)_8$ has only slightly asymmetric bond lengths to Ca (2.510 and 2.499 Å) and a chelate ring completed to one Ca atom but at an extreme distance (2.842 Å) with the third nitrate O atom uncoordinated (Ribár *et al.*, 1973). As in $\text{Ca}(\text{H}_2\text{salpd})(\text{NO}_3)_2$ the bridging atom has the longest bond to N (1.284 Å) but the other two N–O distances are not equal (1.219 and 1.230 Å). There is a similar arrangement (Cameron, Forrest, Taylor & Nuttall, 1971) for bridging $(\text{NO}_3)^-$ in $[\text{Cu}(\text{NO}_3)_2(\text{py})_2]\text{py}$ but here the bridging Cu–O lengths differ considerably (2.042 and 2.542 Å), but as in our compound the two N–O lengths not involved in the bridge are equal (1.228 Å).

Ca–O bond lengths

The eight bonded contacts to Ca cover the range 2.247–2.585 Å; the shortest bonds involve the negatively charged phenolic O atoms and the longest the bridging nitrate ion, $[\text{N}(4)\text{O}_3]^-$. In $\text{Ca}_2(\text{NO}_3)_4(\text{OH}_2)_8$ (Ribár *et al.*, 1973) the five bond lengths to nitrate O atoms vary between 2.477 and 2.853 Å whilst those to water are between 2.414 and 2.475 Å. In diaquabis(L-ascorbato)calcium(II) (Hvoslef & Kjellevoid, 1974) eight O atoms form a distorted square antiprism about Ca, and the bond lengths fall in the range 2.409–2.520 Å.

Infrared spectroscopy of $\text{Ca}(\text{H}_2\text{salpd})(\text{NO}_3)_2$ and related complexes

The complexes listed in Table 1 were prepared by a single method and had very similar appearances. The method is essentially the same as that used in the preparation of the analogous complexes summarized in the *Introduction*, and the metal-ion : Schiff-base ratio in the complexes was varied merely by alterations in the relative amounts of the reagents. These observations tend to suggest that the complexes are structurally related and infrared spectroscopy has confirmed this.

Previously, Bullock & Tajmir-Riahi (1977) had presumed that only the azomethine N atoms were coordinated in complexes of this type, since the C=N stretching vibration increases in frequency on coordination (Mazhar-ul-Haque, Hart & Caughlan, 1970) as in $[\text{N},\text{N}'\text{-ethylene}(\text{pyridine-2-aldimine})\text{-trinitratogadolinium(III)}]$. Similar (but smaller) increases ($\Delta\bar{\nu} = 0\text{--}13\text{ cm}^{-1}$) were found for the Ca

complexes (Table 1). However, it is known (Sandorfy, 1970) that C=N⁺ groups have, in general, higher vibrational frequencies than the parent C=N groups so that the results are consistent with the charge-separated form of the ligand found in this crystallographic study.

The so-called C–O stretch vibration near 1280 cm^{-1} changes little, if at all, among the spectra of the free ligands and those of the Ca (Table 1) and other complexes (Bullock & Tajmir-Riahi, 1977), although this vibration was not observed in $\text{Ca}(\text{H}_2\text{salpd})(\text{NO}_3)_2$ because of interference from a strong, broad nitrate-ion absorption. The C–O stretching vibration must include considerable contributions from the skeletal vibrations of the aromatic ring, and because the vibration changed so little in the complexes it was assumed that the bonding arrangements of the O atoms were the same in the free ligands and the complexes. The C(1)–O(1) length is almost certainly shortened on complex formation but there are profound changes in the neighbouring C–C lengths also, with C(1)–C(2) and C(5)–C(6) longer and C(1)–C(6) shorter than in the free ligand. In addition, the relevant bond angles cannot be the same in the two cases. It is remarkable that the vibrational frequency is almost invariant over a very large number of complexes. Because of the striking similarity between the spectra of the Ca, lanthanoid, and other metal-ion spectra, we assume that the bonding arrangements for the Schiff bases are the same throughout.

The infrared spectrum of $\text{Ca}(\text{H}_2\text{salpd})(\text{NO}_3)_2$ has absorptions at 1483, 1283, 1018 and 820 cm^{-1} , assignable to coordinated nitrate ion (Bullock, 1967) in a low-symmetry environment. It was not possible to predict the presence of two distinct modes of coordination. The remainder of the calcium–nitrate complexes [(ii)–(v), Table 1] with the 2 : 1 ligand : metal-ion stoichiometry had the infrared spectra expected for nitrate ion in approximate $\bar{6}m2$ (D_{3h}) symmetry with a single, broad absorption centred near 1400 cm^{-1} . Unless the nitrate O atoms are identical in their bonding to Ca there is a possibility of lower coordination numbers in the 2 : 1 complexes, although several of these contain solvent molecules which could be coordinated.

The chloro complexes, [(vi)–(ix), Table 1] had very similar spectra to those of the nitrate complexes in the region $1600\text{--}625\text{ cm}^{-1}$ after allowance for nitrate-ion vibrations. There was no strong absorption in the far-infrared spectrum of (viii) in the region $270\text{--}330\text{ cm}^{-1}$ assignable to Ca–Cl vibrations as found (De Bolster & Groeneveld, 1971) at 290 cm^{-1} for dichlorotris(hexamethylphosphoramid)calcium(II).

All the complexes so far examined have very similar spectra in the region $4000\text{--}2000\text{ cm}^{-1}$. The ligand spectra show evidence (Bullock & Tajmir-Riahi, 1977) of strong intramolecular hydrogen bonding, the O–H stretching vibration appearing as a broad band centred at *ca* 2700 cm^{-1} which shifts to *ca* 3000 cm^{-1} in the

spectra of anhydrous nitrate complexes as the hydrogen-bonding arrangements change. In most other cases, however, it is difficult to detect the absorptions of the $O^{\cdots}H^+-N$ system as absorption from solvated molecules (H_2O or $EtOH$) interferes.

References

- ADDISON, C. C., LOGAN, N., WALLWORK, S. C. & GARNER, C. D. (1971). *Q. Rev. Chem. Soc.* **25**, 289–322.
- BULLOCK, J. I. (1967). *J. Inorg. Nucl. Chem.* **29**, 2257–2264.
- BULLOCK, J. I. & TAJMIR-RIAHI, H.-A. (1977). *J. Chem. Soc. Dalton Trans.* pp. 36–39.
- CALLIGARIS, M., NARDIN, G. & RANDACCIO, L. (1971). *Coord. Chem. Rev.* **7**, 385–403.
- CAMERON, A. F., FORREST, K. P., TAYLOR, D. W. & NUTTALL, R. H. (1971). *J. Chem. Soc. A*, pp. 2492–2496.
- CONDORELLI, G., FRAGALA, I., GUIFFRIDA, S. & CASSOL, A. (1975). *Z. Anorg. Allg. Chem.* **412**, 251–257.
- DE BOLSTER, M. W. G. & GROENEVELD, W. L. (1971). *Recl Trav. Chim. Pays-Bas*, **90**, 477–507.
- HOPPE, W. (1965). *Angew. Chem.* **77**, 484–492.
- HVOSLEF, J. & KJELLEVOLD, K. E. (1974). *Acta Cryst.* **B30**, 2711–2716.
- MAZHAR-UL-HAQUE, HART, F. A. & CAUGHLAN, C. N. (1970). *Chem. Commun.* pp. 1240–1241.
- PAHOR, N. B., CALLIGARIS, M., DELISE, P., DODIC, G., NARDIN, G. & RANDACCIO, L. (1976). *J. Chem. Soc. Dalton Trans.* pp. 2478–2483.
- RIBÁR, B., DIVJAKOVIĆ, V., HERAK, R. & PRELESNIK, B. (1973). *Acta Cryst.* **B29**, 1546–1548.
- SANDORFY, C. (1970). *The Chemistry of the Carbon–Nitrogen Double Bond*, edited by S. PATAI, p. 42. New York: Interscience.

Acta Cryst. (1979). **B35**, 2020–2032

The Structure of Triclinic Ferrocene at 101, 123 and 148 K

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Abstract

X-ray diffraction patterns of the low-temperature triclinic modification of ferrocene were recorded from crystals cooled through the transition point at 164 K and also from a single crystal grown below 164 K by sublimation in an evacuated capillary tube, one end of which was warmed, the other cooled by a stream of nitrogen. The diffraction patterns can be indexed in terms of an *F*-centred triclinic cell with $a = 20.960$ (8), $b = 15.019$ (6), $c = 11.421$ (5) Å, $\alpha = 89.47$ (3), $\beta = 119.93$ (3), $\gamma = 90.62$ (3)° (at 101 K), $Z = 16$, where the axial orientation is chosen to correspond to the $P2_1/a$ orientation of the room-temperature monoclinic cell. If the centrosymmetric space group $F\bar{1}$ is assumed, the asymmetric unit consists of two $Fe(C_5H_5)_2$ molecules. Structure analyses were made with data collected at 101, 123 and 148 K. The two $Fe(C_5H_5)_2$ molecules have almost regular pentagonal cyclopentadienyl rings and show virtual D_5 symmetry ($Fe-C$ 2.052, $C-C$ 1.433 Å), the rings being mutually rotated by about 9° from the eclipsed orientation. Some aspects of the thermal-motion analysis, of the crystal packing, and of $X-X$ deformation syntheses are discussed.

Introduction

Ferrocene [bis(cyclopentadienyl)iron] undergoes a phase transition at 164 K (Edwards, Kington & Mason, 1960). The monoclinic high-temperature (HT) phase (space group $P2_1/a$, $Z = 2$) is disordered, and the nature of this disorder has only recently been clarified by X-ray and neutron diffraction studies at temperatures above and below the transition point (Seiler & Dunitz, 1979; Takusagawa & Koetzle, 1979). These studies show that the centrosymmetric structure formerly assigned to the ferrocene molecule in the crystalline state (Dunitz & Orgel, 1953; Dunitz, Orgel & Rich, 1956) is incorrect. As a consequence of the crystal disorder, individual ferrocene molecules need not have the molecular inversion centres that would be required by the space-group symmetry in an ordered structure; indeed, the new interpretations of both electron and nuclear scattering distributions in terms of superposition structures led to the conclusion that the conformation of the ferrocene molecules in the crystal was neither staggered (D_{5d}) nor eclipsed (D_{5h}) but intermediate (D_5).

In our earlier paper (Seiler & Dunitz, 1979) we drew on some results of a preliminary analysis of the low-