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The 2,5,8,11,14-pentaoxaheptadecane (tetraglyme) adducts of barium complexes of 1,1,1,5,5,5-hexafluoro-2,4-pentanedione (H(hfacac)), 1,1,1-trifluoro-2,4-pentanedione (H(tfacac)) and 2,2,6,6-tetramethyl-3,5-heptanedione (H(thd)) have been prepared and characterized by X-ray crystallography, ¹H and ¹³C nmr spectroscopies, melting and sublimation points, and elemental analysis. The thermal stability of the complexes is related to their solid state structure in which the coordination number around the barium atom is nine with a monocapped, twisted square prism structure. Metalorganic chemical vapor deposition experiments were performed using the 1,1,1,5,5,5-hexafluoro-2,4-pentanedionato and 1,1,1-trifluoro-2,4-pentanedionato complexes; the 2,2,6,6-tetramethyl-3,5-heptanedionato complex dissociated prior to sublimation. The as-deposited barium fluoride films were characterized by scanning electron microscopy and energy dispersive x-ray spectroscopy.

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Volatile Barium β -Diketonate Polyether Adducts.
Synthesis, Characterization and Metalorganic Chemical Vapor Deposition

by

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**Volatile, Barium β -Diketonate Polyether Adducts.
Synthesis, Characterization and Metalorganic Chemical Vapor Deposition.**

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Abstract

The 2,5,8,11,14-pentaoxaheptadecane (tetraglyme) adducts of barium complexes of 1,1,1,5,5,5-hexafluoro-2,4-pentanedione (H(hfacac)), 1,1,1-trifluoro-2,4-pentanedione (H[tfacac]) and 2,2,6,6-tetramethyl-3,5-heptanedione (H(thd)) have been prepared and characterized by X-ray crystallography, ^1H and ^{13}C nmr spectroscopies, melting and sublimation points, and elemental analysis. The thermal stability of the complexes is related to their solid state structure in which the coordination number around the barium atom is nine with a monocapped, twisted square prism structure. Metalorganic chemical vapor deposition experiments were performed using the 1,1,1,5,5,5-hexafluoro-2,4-pentanedionato and 1,1,1-trifluoro-2,4-pentanedionato complexes; the 2,2,6,6-tetramethyl-3,5-heptanedionato complex dissociated prior to sublimation. The as-deposited barium fluoride films were characterized by scanning electron microscopy and energy dispersive x-ray spectroscopy.

Introduction

Since the discovery of superconductivity above 30K in 1986¹ numerous research efforts have focused on thin film preparation of these materials for microelectronic applications. Metalorganic Chemical Vapor Deposition (MOCVD) has significant advantages relative to physical vapor deposition (PVD) methods in the growth of superconducting thin films; large wafers can be uniformly coated and scale up to large volumes is easily accomplished. MOCVD

also allows for the exacting control of the film microstructure and stoichiometry which is essential for the manufacture of superconducting devices with optimal and reproducible properties. Uniform films of BiSrCaCuO have already been grown over large areas (45 cm²) by MOCVD² but these films required a high temperature ($T > 850^{\circ}\text{C}$) anneal to become superconducting. Plasma enhanced-MOCVD (PE-MOCVD) of high temperature superconducting thin films has been reported by several groups^{3,4,5,6} at temperatures ($570^{\circ}\text{C} \leq T \leq 700^{\circ}\text{C}$) which are compatible with standard silicon integrated circuit process technology.

The primary obstacle to the widespread application of MOCVD to the growth of high T_c superconducting oxide thin films (YBaCuO, BiCaSrCuO, TlBaCaCuO) is the absence of an effective alkali metal, in particular barium, source reagent. Barium prefers high coordination numbers, up to 12,⁷ and the lack of steric saturation of many barium organometallic complexes leads them to be strongly associated in the solid state; barium organometallics often undergo thermal decomposition before vaporization.⁸ For example, barium β -diketonates ($\text{Ba}(\text{RCOCH}_2\text{COR}')_2$ where $\text{R}, \text{R}' = \text{CH}_3$) have low solubility and thermal decomposition during sublimation is great. The use of large, sterically bulky groups ($\text{R}, \text{R}' = (\text{CH}_3)_3\text{C}$, and $\text{R} = (\text{CH}_3)_3\text{C}$, $\text{R}' = \text{C}_3\text{F}_7$) to block open barium coordination sites reduces intermolecular interactions, increases solubility even in non polar solvents, and enhances volatility of the complexes.⁹ Even with bulky ligands the barium atom is still not coordinatively saturated. The current MOCVD precursors for barium (barium 1,1,1,2,2,3,3-heptafluoro-7,7-dimethyloctane-4,6-dionate ($\text{Ba}(\text{fod})_2$), and barium 2,2,6,6-tetramethyl-3,5-heptanedionate ($\text{Ba}(\text{thd})_2$) undergo partial decomposition at the temperatures ($> 200^{\circ}\text{C}$) required to sustain sufficient usable vapor pressure.^{10,11,12} Furthermore, association in the gas phase¹³ leads to fluctuations in element delivery rates.

Improved stability of barium transport has been accomplished by saturating the carrier gas stream going to the $\text{Ba}(\text{thd})_2$ source with the 2,2,6,6-tetramethyl-3,5-heptanedione vapor.¹⁴ Similarly, saturating the carrier gas with oxygen or nitrogen Lewis bases can lower the required bubbler temperature.

Tetrahydrofuran (THF) lowers the reagent bubbler temperature from 300°C to 180°C ¹⁵ and transport of a number of barium β -diketonates at temperatures as low as 150°C has been achieved by adding nitrogen Lewis bases (e. g., triethylamine) to the carrier gas.¹⁶ Excess hydrocarbons can lead to the co-deposition of carbon

and compete for surface sites thus interfering with the *in-situ* deposition of the high temperature superconductors. Consequently, a mononuclear barium source reagent with a vapor pressure of ~1 Torr at 150°C which is thermally stable at its vaporization temperature would simplify MOCVD process development and increase process reproducibility and control.

Our investigations have concentrated on the the factors affecting the volatility, stability and deposition chemistry of the barium complexes which determine their potential as MOCVD source reagents. We report here the synthesis and characterization of three barium β -diketonate:tetraglyme adducts, and preliminary MOCVD film growth results.

Experimental section

General Information. Synthesis and handling of all organometallic complexes was performed under nitrogen atmosphere using standard Schlenk techniques or in a Vacuum Atmospheres inert atmosphere glove box. Tetraglyme was distilled over Na/K alloy and stored over calcium hydride. Barium hydride, 1,1,1,5,5,5-hexafluoro-2,4-pentanedione, 1,1,1-trifluoro-2,4-pentanedione (Strem Chemicals) and 2,2,6,6-tetramethyl-3,5-heptanedione (Aldrich Chemical Co.) were used as received. ^1H nmr and ^{13}C nmr spectra were measured with an IBM WP200SY spectrometer. Chemical shifts are reported in ppm on a δ scale with residual resonances from the nmr solvents serving as internal standards for the ^1H (C_6D_6 δ = 7.15 ppm) and ^{13}C (C_6D_6 δ = 128.0 ppm) spectra. Elemental analysis were obtained from Galbriath Laboratories Inc., 2323 Sycamore Drive, Knoxville, TN 37921-1750.

Synthesis

Preparation of barium bis(1,1,1,5,5,5-hexafluoro-2,4-pentanedionate)·tetraglyme adduct ($\text{Ba}(\text{hfacac})_2 \cdot (\text{CH}_3\text{O}(\text{CH}_2\text{CH}_2\text{O})_4\text{CH}_3)$) · 1. 1,1,1,5,5,5-hexafluoro-2,4-pentanedione (14.74 g, 70 mmoles) was added to a stirring suspension of barium hydride (11.36 g, 35.0 mmoles) in tetraglyme. Gas was constantly evolved throughout the addition of the β -diketone. The resulting, yellow solution was decanted from a white crystalline solid (11.3 g, 42%). The solid was then washed

with ~ 50ml of cold pentane and dried under vacuum (0.2 Torr). The final product (10.9 g, 40%, m.p. 121-125°C) was purified by vacuum sublimation at 150°C and 0.2 Torr. Anal. Calcd (found) for $\text{BaC}_{20}\text{F}_{12}\text{H}_{24}\text{O}_9$: Ba, 17.75 (17.65); C, 31.05 (31.44); F, 29.47 (28.09); H, 3.13 (3.32). NMR ^1H (C_6D_6), δ 3.04 (m, 6H), 3.15 (m, 12H), 3.30 (m, 4H), 6.28 (s, 2H) ppm. ^{13}C , δ 58.98 ($\underline{\text{CH}}$), 70.37 ($\underline{\text{CH}_2}$), 70.73 ($\underline{\text{CH}_2}$), 71.51 ($\underline{\text{CH}_3}$), 87.66 ($\underline{\text{CF}_3}$) ppm.

Preparation of barium bis(1,1,1-trifluoro-2,4-pentanedionate)-(tetraglyme) adduct ($\text{Ba}(\text{tfacac})_2 \cdot (\text{CH}_3\text{O}(\text{CH}_2\text{CH}_2\text{O})_4\text{CH}_3)$) - 2. 1,1,1-trifluoro-2,4-pentanedione (5.0 g, 32.4 mmoles) was added dropwise via syringe to a stirring slurry of barium hydride (2.26 g, 16.1 mmoles) in tetraglyme. Gas was constantly evolved throughout the addition of the β -diketone. The reaction mixture was then stirred overnight and the resulting mixture was filtered to leave a white crystalline solid and an orange filtrate. The solid was washed with cold pentane and then dried in a nitrogen purge (4.2 g, 40%). 0.95 g of the crude material was sublimed at 150°C and 0.1 Torr to yield a white solid (0.60 g, 25%, m.p. 133-136°C). Anal. Calcd (found) for $\text{BaC}_{20}\text{F}_6\text{H}_{30}\text{O}_9$: Ba, 20.63 (20.52); C, 36.08 (36.55); F, 17.12 (16.94); H, 4.54 (4.54). NMR ^1H (C_6D_6), δ 1.88 (s, 6H) 2.93 (s, 6H), 3.16 (m, 4H), 3.36 (br. s, 12H), 5.83 (s, 2H) ppm. ^{13}C , δ 29.85 ($\underline{\text{CH}_3}$), 59.17 ($\underline{\text{CH}}$), 70.01 ($\underline{\text{CH}_2}$), 70.11 ($\underline{\text{CH}_2}$), 70.50 ($\underline{\text{CH}_2}$), 71.12 ($\underline{\text{CH}_3}$), 93.28 ($\underline{\text{CF}_3}$), 194.06 ($\underline{\text{C=O}}$) ppm.

Preparation of barium bis(2,2,6,6-tetramethyl-3,5-heptanedionate)-(tetraglyme) adduct ($\text{Ba}(\text{thd})_2 \cdot (\text{CH}_3\text{O}(\text{CH}_2\text{CH}_2\text{O})_4\text{CH}_3)$) - 3. 2,2,6,6-tetramethyl-3,5-heptanedione (2.65 g, 14.0 mmoles) was added to a stirring suspension of barium hydride (1.0 g, 70 mmoles) in ~ 2Jml of tetraglyme; gas evolution starting immediately after the β -diketone was added and continued throughout the addition. The reaction mixture was stirred overnight to yield a cream colored solid and a pale yellow solution. The solid was filtered, washed with cold pentane and then dried under vacuum (0.2 Torr) yielding a white solid (1.04 g, 27%, m.p. 93-97°C). Anal. Calcd (found) for $\text{BaC}_{32}\text{H}_{60}\text{O}_9$: Ba, 19.83 (19.91); C, 52.93 (49.74); H, 8.33 (7.87); O, 18.91 (18.61). NMR ^1H (C_6D_6), δ 1.39 (s, 36H) 3.10 (br. s, 6H), 3.29 (m, 4H), 3.36 (br. s, 12H), 5.85 (s, 2H) ppm. ^{13}C , δ 29.78, 29.66 ($(\underline{\text{CH}_3})_3\text{C}$), 41.10 ($(\underline{\text{CH}_3})_3\text{C}$), 59.15 ($\underline{\text{CH}}$), 70.41 ($\underline{\text{CH}_2}$), 70.59 ($\underline{\text{CH}_2}$), 71.66 ($\underline{\text{CH}_3}$), 197.50 ($\underline{\text{C=O}}$) ppm.

Vapor Pressure Measurements. The vapor pressure of 1 and 2 were measured with the apparatus illustrated in Figure 1. The sample cylinder was loaded with

1.0 g of precursor in an inert atmosphere. The cylinder was then connected to the system which was subsequently evacuated and backfilled with nitrogen three times. The entire system was then evacuated, the oven temperature was set and the system was allowed to equilibrate with valves 1, 2 and 3 open to vacuum. Valve 3 was then closed and 4 opened and a pressure reading was taken after equilibration (1-2 hrs). After each measurement valve 4 was closed and 3 opened and a background reading to be taken. The vapor pressure was calculated as the difference between the total system and background pressures. The system was calibrated using the vapor pressure curve for tetraethyleneglycol.¹⁷

Vapor Pressure Results

The vapor pressure of 1 and 2 were measured at several temperatures from 120 to 180°C. The data were fit by a simple linear least squares analysis to equation 1a and b (correlation 0.893 for equation 1a and 0.938 for 1b) which are plotted in figures 2 a and b.

$$\ln P_1 (\text{torr}) = 21.875 - 9.0273 \times 10^3 / T \quad 1a$$

$$\ln P_2 (\text{torr}) = 27.477 - 1.1989 \times 10^4 / T \quad 1b$$

The values of $\Delta H_{\text{sub}}^\circ$ of 1.09 and 1.44 kJmol⁻¹ are found for the heats of sublimation for 1 and 2, respectively¹⁸.

MOCVD Experiments. Reduced pressure MOCVD experiments were carried out in a standard horizontal hot wall reactor (Figure 3). The precursor (0.5 g) was loaded into the reagent bubbler in an inert atmosphere and connected to the system without exposing the compound to air. The system was evacuated to 0.05 Torr and bubbler temperature was raised to 175°C. The nitrogen carrier gas flow, regulated by an MKS mass flow controller, was 10 cm³ min⁻¹ and the total system pressure was maintained at 4 Torr. The reagent was transported through heated lines to the quartz reactor tube which was maintained at 650°C. A typical growth run lasted 2 hrs and the film deposited on the inner wall of the quartz tube was characterized by scanning electron microscopy (SEM) and energy dispersive x-ray analysis (EDX).

Single Crystal X-ray Analysis. The data collection was performed on a Nicolet R3m diffractometer and the computer programs and the sources of the scattering factors which were taken from the SHELXTL program library (5.1).¹⁹ Colorless crystals of **1** were obtained by reduced pressure sublimation, those of **2** and **3** by slow evaporation of a toluene solution. The crystals were mounted on glass fibers with epoxy cement. The basic crystallographic parameters obtained are listed in Table I. The unit cell parameters were obtained from the least-squares fit of 25 reflections ($20^\circ \leq \theta \leq 25^\circ$). The structure of **1** was solved by direct methods which located the barium atom. **2** and **3** were each solved using Patterson maps which located the barium atoms. The remaining non-hydrogen atoms were located from subsequent difference Fourier syntheses. All hydrogen atoms were included as idealized isotropic contributions ($d(\text{CH}) = 0.960 \text{ \AA}$; $U = 1.2U$ for attached C). For **1** and **2** all non-hydrogens atoms were refined with anisotropic thermal parameters. For **3** all atoms were refined anisotropically except in one *t*-butyl group, which is disordered, where only the carbon atoms with the greater contribution to the occupancy (77%) were refined anisotropically.

Results and Discussion

Our search for barium source reagents with improved volatility and deposition chemistry has been based on a simple premise; mononuclear barium complexes require filled coordination spheres. Research into blocking the open coordination sites using multidentate Lewis bases to reduce intermolecular interactions and increase volatility has met with some success.²⁰

N,N,N',N'-tetramethylethylenediamine has been used to complex with Group II alkoxides to promote solubility.²¹ A similar increase in solubility of barium bis(pentamethylcyclopentadienide) over barium bis(cyclopentadienide) caused by the bulky pentamethylcyclopentadienide ligand has also been reported.²²

Investigations into coordination of β -diketonates with diamines and triamines lead to the formation of a number of isolated adducts²³ which were stable at room temperature but decomposed at higher temperatures ($>100^\circ\text{C}$) to yield the free amine and the parent β -diketonate.

Adducts of Group II bis(1,1,1,5,5,5-hexafluoro-2,4-pentanedionates) with the general formula $M(\text{CF}_3\text{COCHCOCF}_3)_2 \cdot (\text{CH}_3\text{O}(\text{CH}_2\text{CH}_2\text{O})_n\text{CH}_3)$ ($M = \text{Ca}, \text{Sr}, \text{Ba}$ and $n = 1$) have been prepared by Spee. Coordination of the longer polyethers ($n = 4, 5$) dramatically enhanced the volatility of the barium complexes.²⁴ For example, $\text{Ba}(\text{CF}_3\text{COCHCOCF}_3)_2$ ($\text{Ba}(\text{hfacac})_2$) is not volatile below 205°C at 10^{-5} Torr,²⁵ whereas the $\text{Ba}(\text{CF}_3\text{COCHCOCF}_3)_2 \cdot (\text{CH}_3\text{O}(\text{CH}_2\text{CH}_2\text{O})_4\text{CH}_3)$ ($\text{Ba}(\text{tfacac})_2 \cdot (\text{tetraglyme})$) adduct sublimes readily at 120°C at 10^{-2} Torr. Similarly, $\text{Ba}(\text{CH}_3\text{COCHCOCF}_3)_2 \cdot (\text{CH}_3\text{O}(\text{CH}_2\text{CH}_2\text{O})_4\text{CH}_3)$ ($\text{Ba}(\text{tfacac})_2 \cdot (\text{tetraglyme})$) sublimes at 150°C at 10^{-2} Torr. Vapor pressure measurements showed that the complexes were well behaved and were considerably more volatile than the parent β -diketonate complexes.

Although both $\text{Ba}(\text{tfacac})_2$ and $\text{Ba}(\text{hfacac})_2$ are not soluble in non-coordinating solvents, the respective tetraglyme adducts dissolve readily in benzene. The barium β -diketonate/tetraglyme complexes are not hygroscopic. Coordinated water has been reported to cause instabilities in the vapor pressure of the barium complexes because the rate of water dissociation competes favorably with complex sublimation.

ORTEP diagrams (Figure 4 a, b and c) show the average Ba-O bond distance in **1**, **2** and **3** differs only slightly, being 2.782(6), 2.788(4), 2.799(5) Å, respectively. The average distances for Ba to the β -diketonate oxygen atoms are 2.705(5), 2.691(3), and 2.683(4) Å, and the Ba to tetraglyme oxygen atoms are 2.837(7), 2.867(4), and 2.893(5) Å, respectively (Table II). In **1** the plane of Ba, O(1), O(2) is $19.3(2)^\circ$ from the plane of Ba, O(3) and O(4) and in **2** the plane of Ba, O(6), O(7) is $21.4(2)^\circ$ from the plane of Ba, O(8) and O(9). The same twisted propeller shape is seen in all three structures but in **3** the angle between the plane of Ba, O(3), O(4) and Ba, O(1) and O(2) is $29.6(2)^\circ$ (Table III). This is possibly due to the steric bulk of the tertiary butyl groups at the 1 and 5 positions and may also account for the different position of the terminal methyl groups in the tetraglyme molecule. The ^{13}C nmr spectra show an increasing upfield shift in the methylene signals of the coordinated tetraglyme from **1** > **2** > **3** away from the parent polyether. This shift is indicative of the strength of coordination showing it to be weakest in $\text{Ba}(\text{thd})_2 \cdot (\text{tetraglyme})$.

Tetraglyme coordination appears more affected by the size of the R substituents than the electronegativity of the β -diketonate itself. Van der Waals repulsion of the terminal methyl groups of the tetraglyme molecule with the tertiary butyl groups of the $\text{Ba}(\text{thd})_2$ weakens the coordination of the tetraglyme with the barium atom. $\text{Ba}(\text{thd})_2 \cdot (\text{tetraglyme})$ decomposed at 110°C (0.1 Torr) to give the parent β -diketonate and tetraglyme. Preliminary experiments have been carried out with the highly sterically hindered but highly electronegative barium bis(2,2-dimethyl-6,6,7,7,8,8,8-heptafluoro-3,5-octanedionate). The tetraglyme adduct was isolated as an impure oil which dissociated at 100°C and 10^{-2} Torr to yield the parent β -diketonate and tetraglyme. Further experiments are in progress to evaluate the relative contributions of steric and electronic effects arising from the structure of the β -diketonates to the strength of coordination of tetraglyme to the β -diketonate complexes of barium.

MOCVD Results

The increased thermal stability and vapor pressure of $\text{Ba}(\text{hfacac})_2 \cdot (\text{tetraglyme})$ and $\text{Ba}(\text{tfacac})_2 \cdot (\text{tetraglyme})$ enabled their use as MOCVD source reagents. Films were deposited at $0.2 \mu\text{h}^{-1}$ on the inner wall of a quartz tube. All films were dense (Figure 5 a and b). EDX analysis indicated that the films were barium fluoride contaminated with a trace of carbon. The carbon presumably arose from the fragmentation and incorporation of the organic ligands (Figure 6 a and b). $\text{Ba}(\text{hfacac})_2$ reacts to give barium fluoride under similar conditions and the as-deposited films grown using the tetraglyme adducts do not differ in composition. Tetraglyme did not effect the formation of barium fluoride films; the formation of barium fluoride films from the decomposition of fluorine containing β -diketonates at temperatures between 500 and 700°C is well documented.^{10,25,26}

Conclusion.

We have synthesized and characterized tetraglyme adducts of barium bis(1,1,1,5,5,5-hexafluoro-2,4-pentanedionate), barium bis(1,1,1-trifluoro-2,4-pentanedionate) and barium bis(2,2,6,6-tetramethyl-3,5-heptanedionate). The fluorine containing complexes $\text{Ba}(\text{hfacac})_2 \cdot (\text{tetraglyme})$ (vapor pressure of 0.23

Torr at 150°C) and Ba(tfacac)₂·(tetraglyme) (vapor pressure of 0.06 Torr at 150°C) have been used to grow barium fluoride films. The decomposition of the non-fluorinated Ba(thd)₂·(CH₃O(CH₂CH₂O)₄CH₃) before sublimation is attributed to the steric hindrance of the t-butyl groups.

The presence of fluorine in the β-diketonate results in the complexes decomposing to barium fluoride. Barium fluoride is thermally stable below 1000°C and the MOCVD of *in situ* superconducting YBaCuO and TlBaCaCuO thin films requires a non-fluorine containing complex. Investigations are currently underway to synthesize stable complexes with the general formula Ba(RCOCHCOR')₂·(CH₃O(CH₂CH₂O)_nCH₃) where R and R' are non fluorinated alkyl groups. These complexes will replace current Ba MOCVD reagents as they require lower temperatures for sublimation; are stable at their sublimation temperature and have higher vapor pressure enabling superior transport.

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Supplementary Material Available: Listings of atomic coordinates and isotropic thermal parameters for 1, 2 and 3. Ordering information is given on any current masthead page.

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$$dP/dT = (\Delta H_{\text{sub}}^{\circ}) / (RT^2).$$
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Figure 1. Diagram of apparatus used to measure vapor pressure

Figure 2a. Vapor pressure plot for $\text{Ba}(\text{CF}_3\text{COCHCOCF}_3)_2 \cdot (\text{CHO}(\text{CH}_2\text{CH}_2\text{O})\text{CH}_3)$

Figure 2b. Vapor pressure plot for $\text{Ba}(\text{CF}_3\text{COCHCOCH}_3)_2 \cdot (\text{CHO}(\text{CH}_2\text{CH}_2\text{O})\text{CH}_3)$

Figure 3. Diagram of horizontal hot wall reactor used to deposit barium fluoride films.

Figure 4a. ORTEP plot of $\text{BaC}_{20}\text{H}_{24}\text{F}_{12}\text{O}_9$ (1). H atoms are omitted for clarity.

Figure 4b. ORTEP plot of $\text{BaC}_{20}\text{H}_{30}\text{F}_6\text{O}_9$ (2). H atoms are omitted for clarity.

Figure 4c. ORTEP plot of $\text{BaC}_{20}\text{H}_{60}\text{O}_9$ (3). H atoms are omitted for clarity.

Figure 5a. Scanning Electron Micrograph of film deposited using $\text{Ba}(\text{CF}_3\text{COCHCOCF}_3)_2 \cdot (\text{CHO}(\text{CH}_2\text{CH}_2\text{O})\text{CH}_3)$.

Figure 5b. Scanning Electron Micrograph of film deposited using $\text{Ba}(\text{CF}_3\text{COCHCOCH}_3)_2 \cdot (\text{CHO}(\text{CH}_2\text{CH}_2\text{O})\text{CH}_3)$.

Figure 6a. Energy Dispersive X-ray analysis of film deposited using $\text{Ba}(\text{CF}_3\text{COCHCOCF}_3)_2 \cdot (\text{CHO}(\text{CH}_2\text{CH}_2\text{O})\text{CH}_3)$.

Figure 6b. Energy Dispersive X-ray analysis of film deposited using $\text{Ba}(\text{CF}_3\text{COCHCOCH}_3)_2 \cdot (\text{CHO}(\text{CH}_2\text{CH}_2\text{O})\text{CH}_3)$.

Table I. Crystallographic data for 1, 2 and 3.

Table II. Bond distances (Å) for 1, 2 and 3.

Table III. Bond angles (degrees) for 1, 2 and 3.

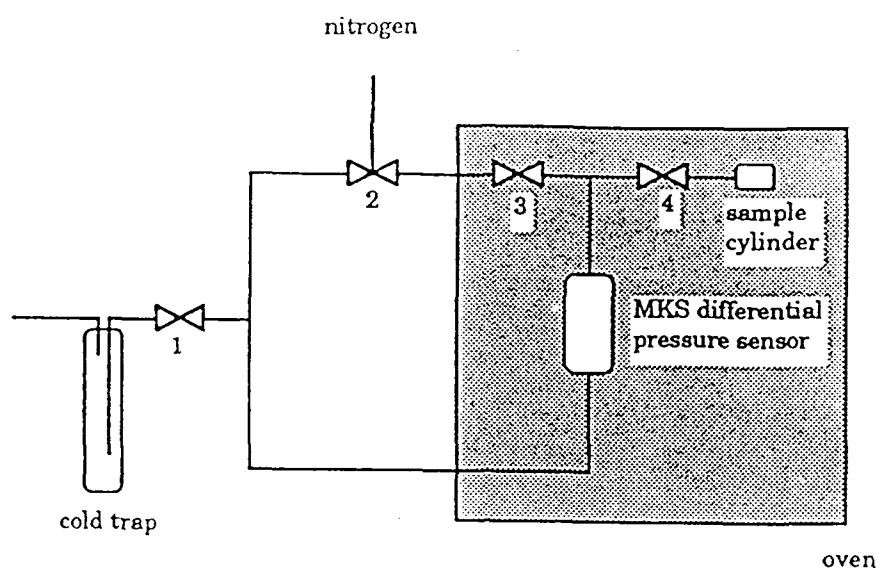


Fig 1 - GORENCE et al

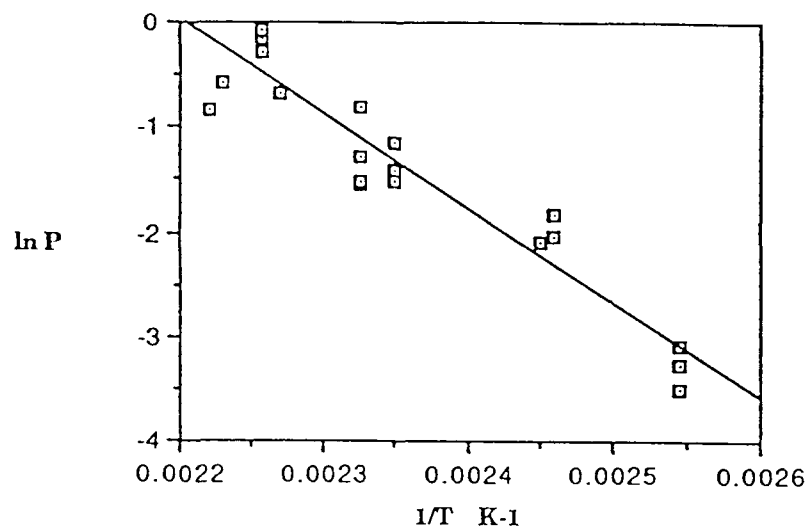


Fig 2a - GARDNER et al

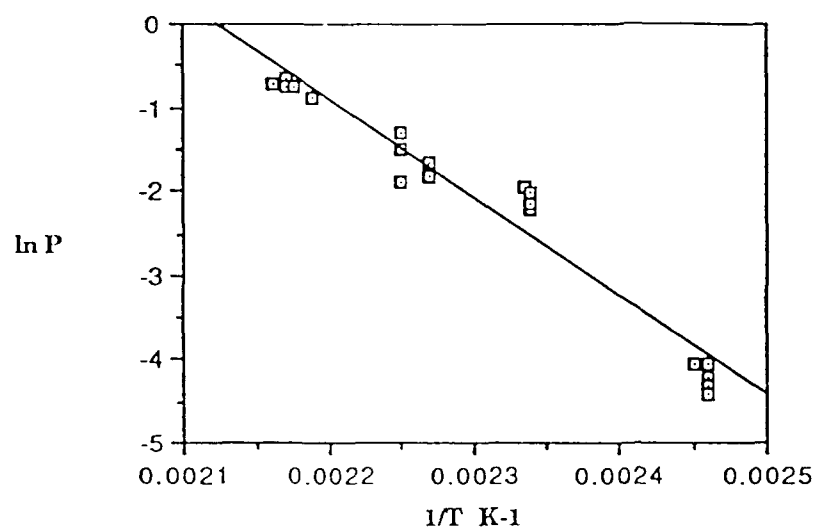


Fig 2b Graph of $\ln P$ vs $1/T$

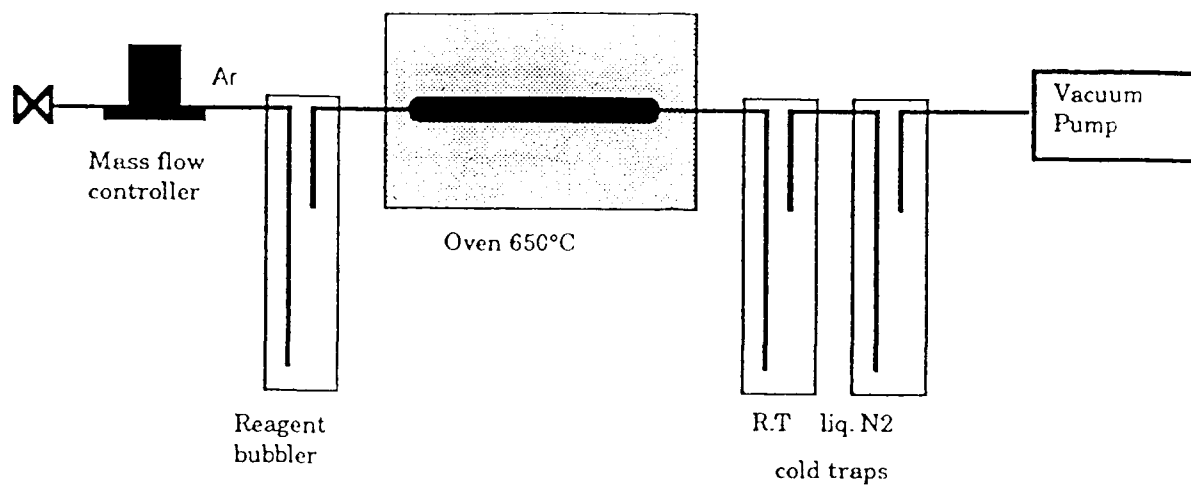
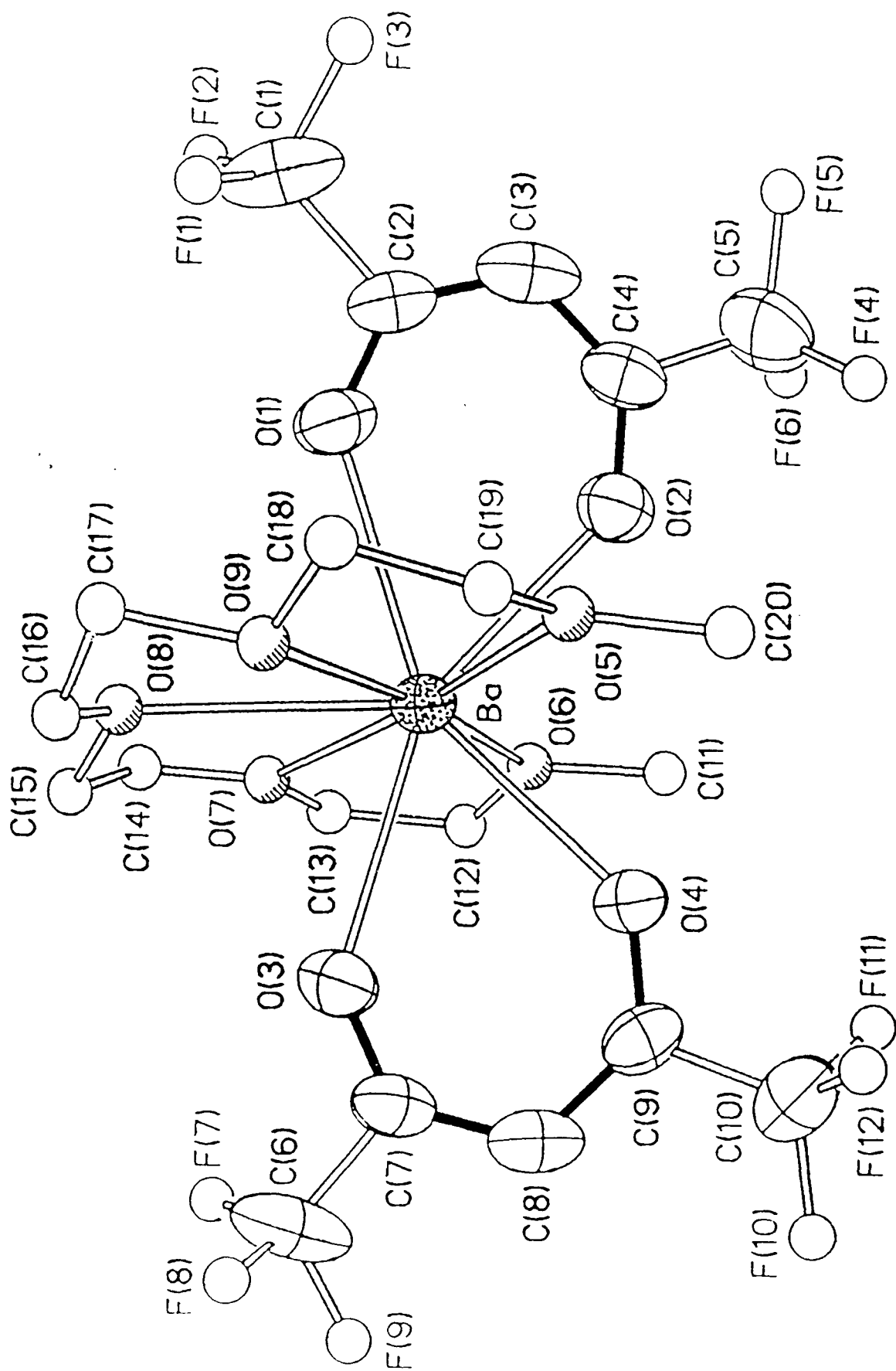
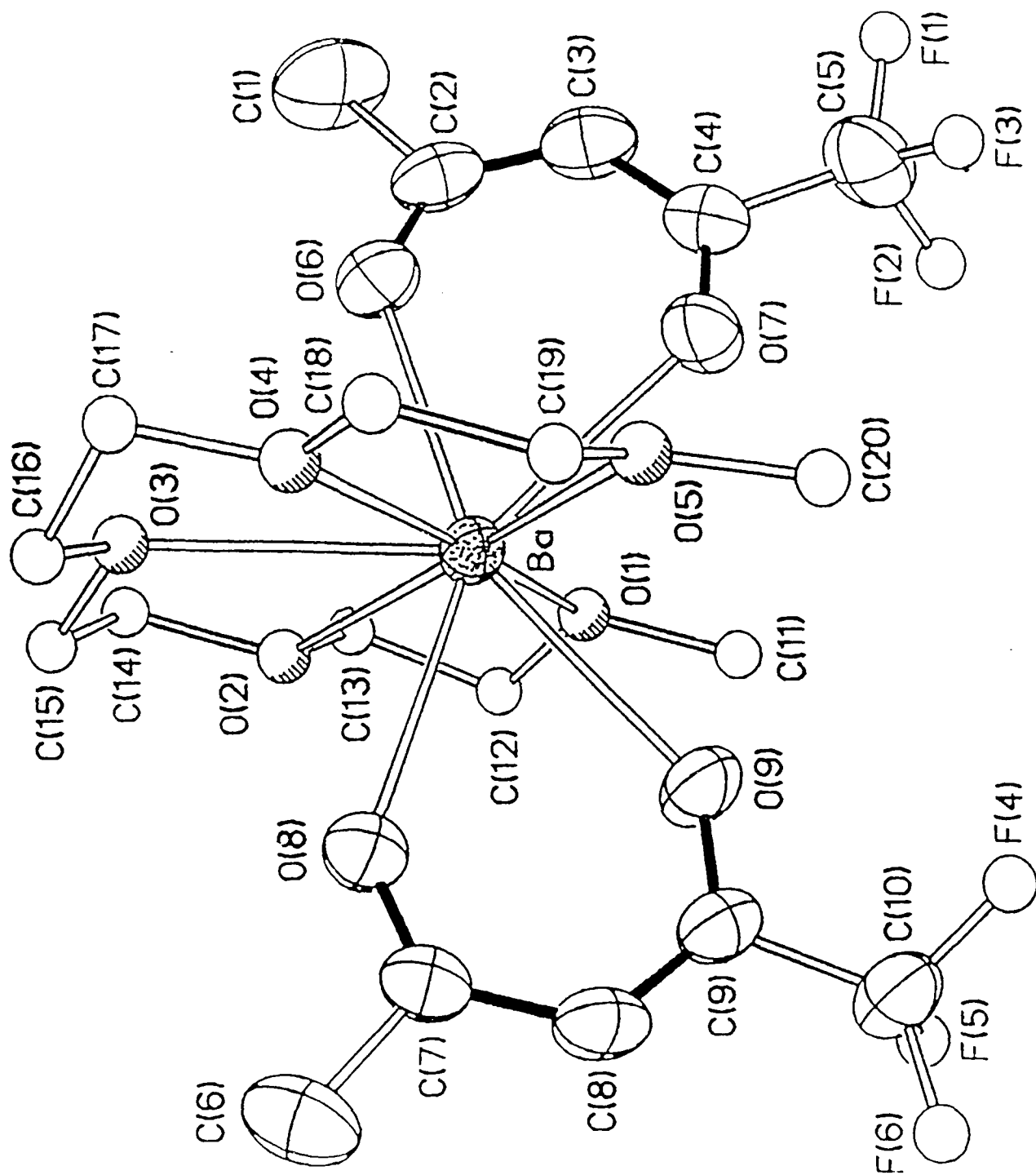
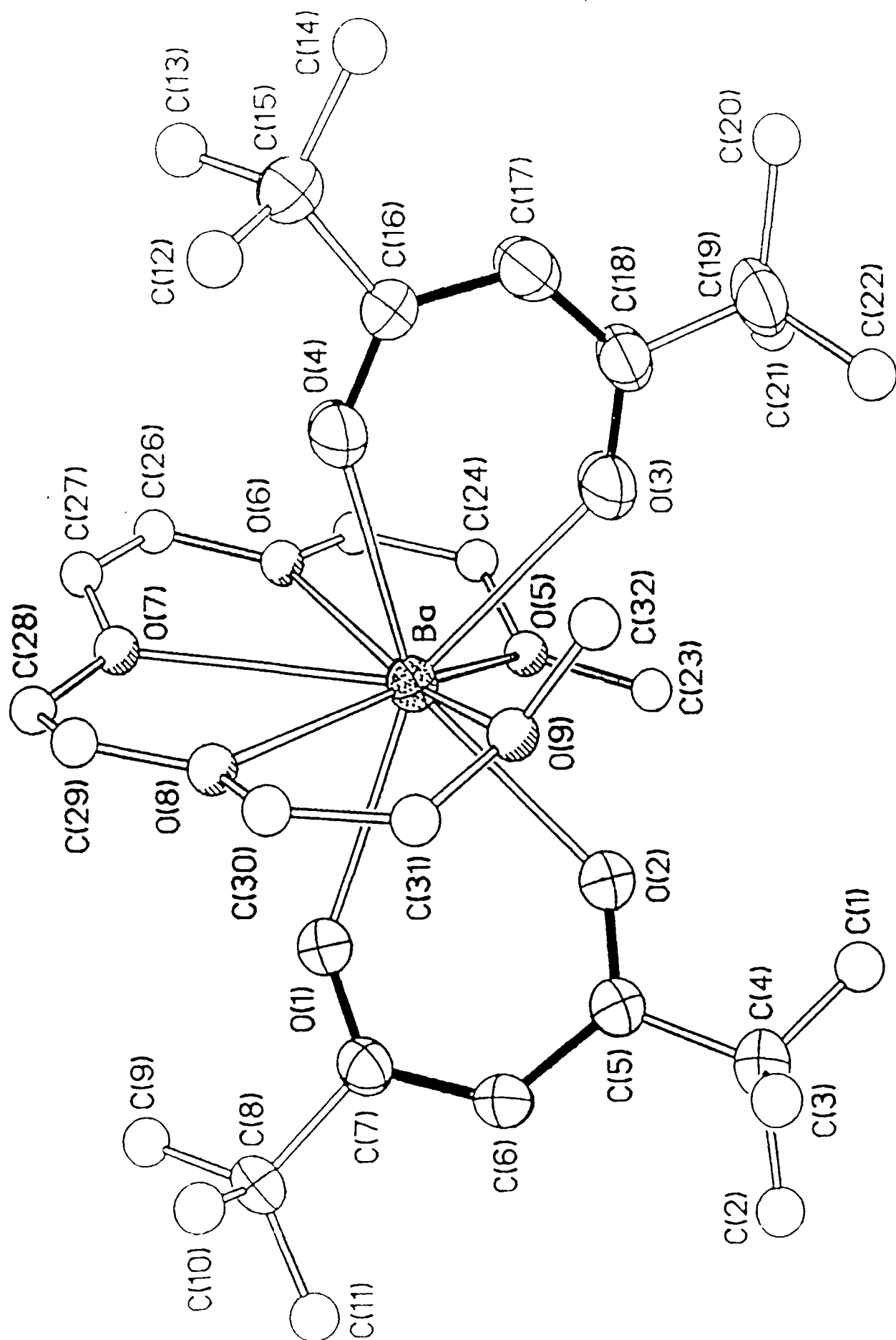


Fig. 3. Gatenbeck et al.

10 for 3.31.70 (L) - 0.7 b13

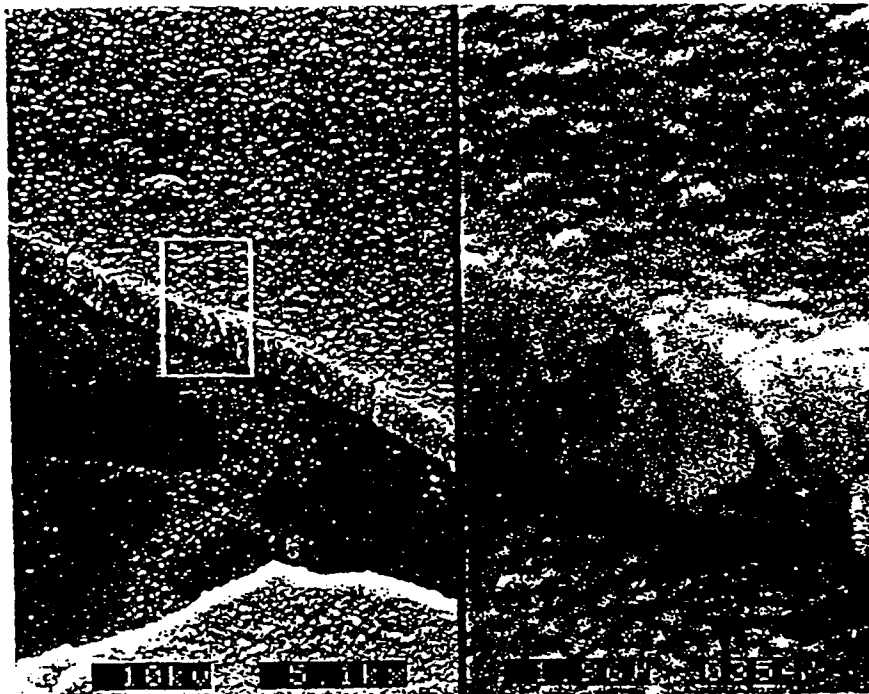






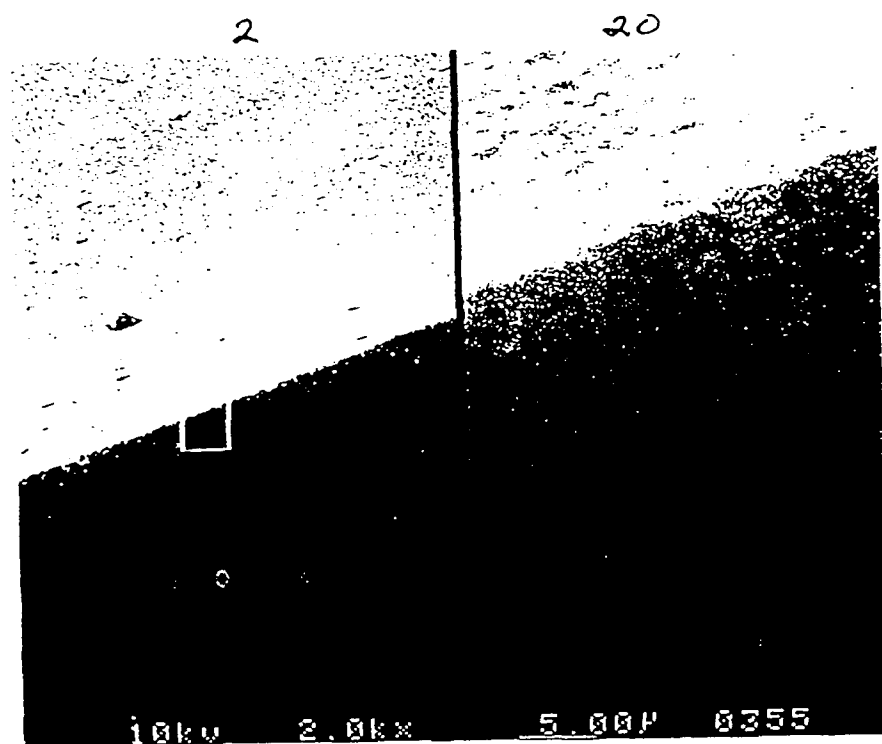
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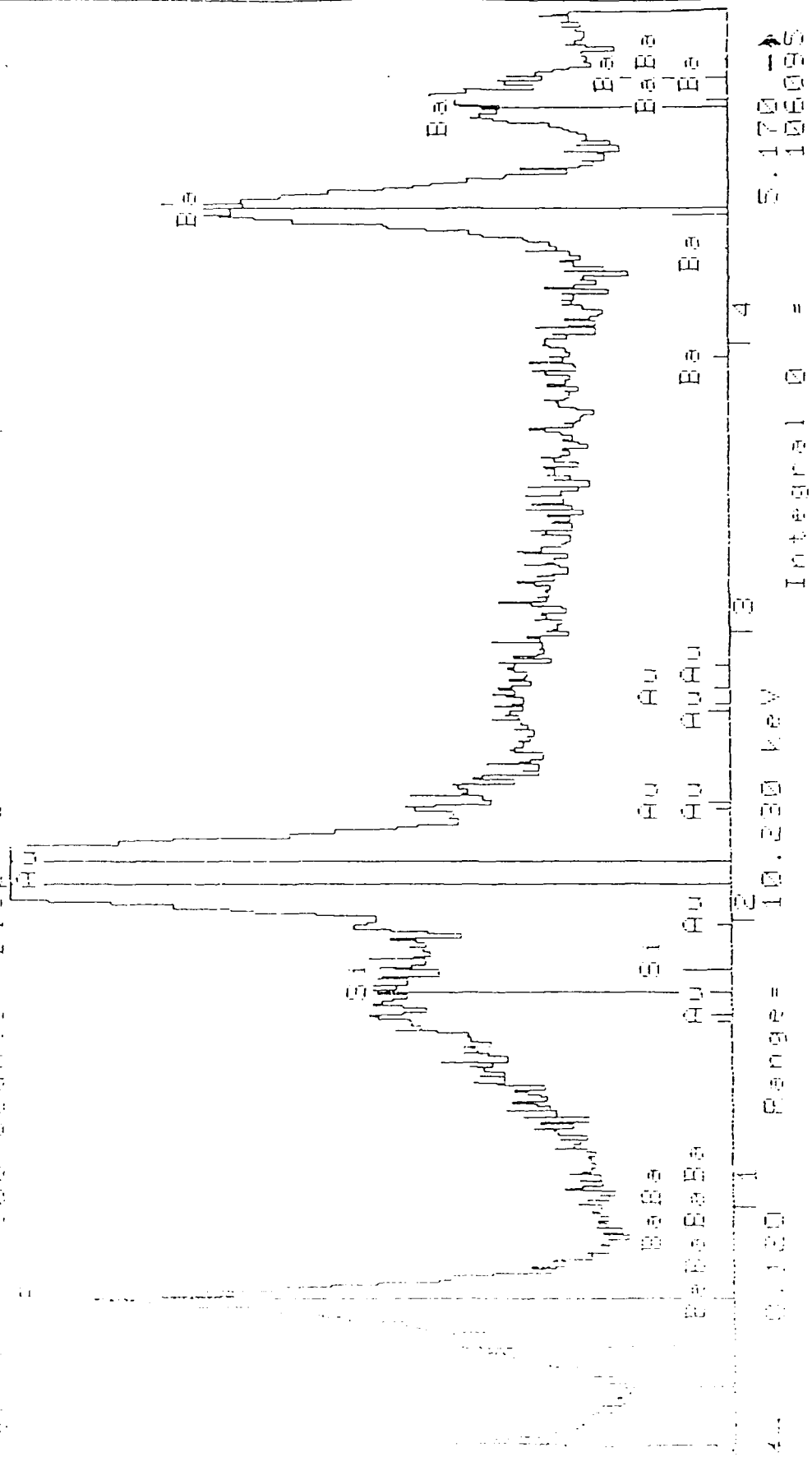
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48 sec



1991 14:48:33

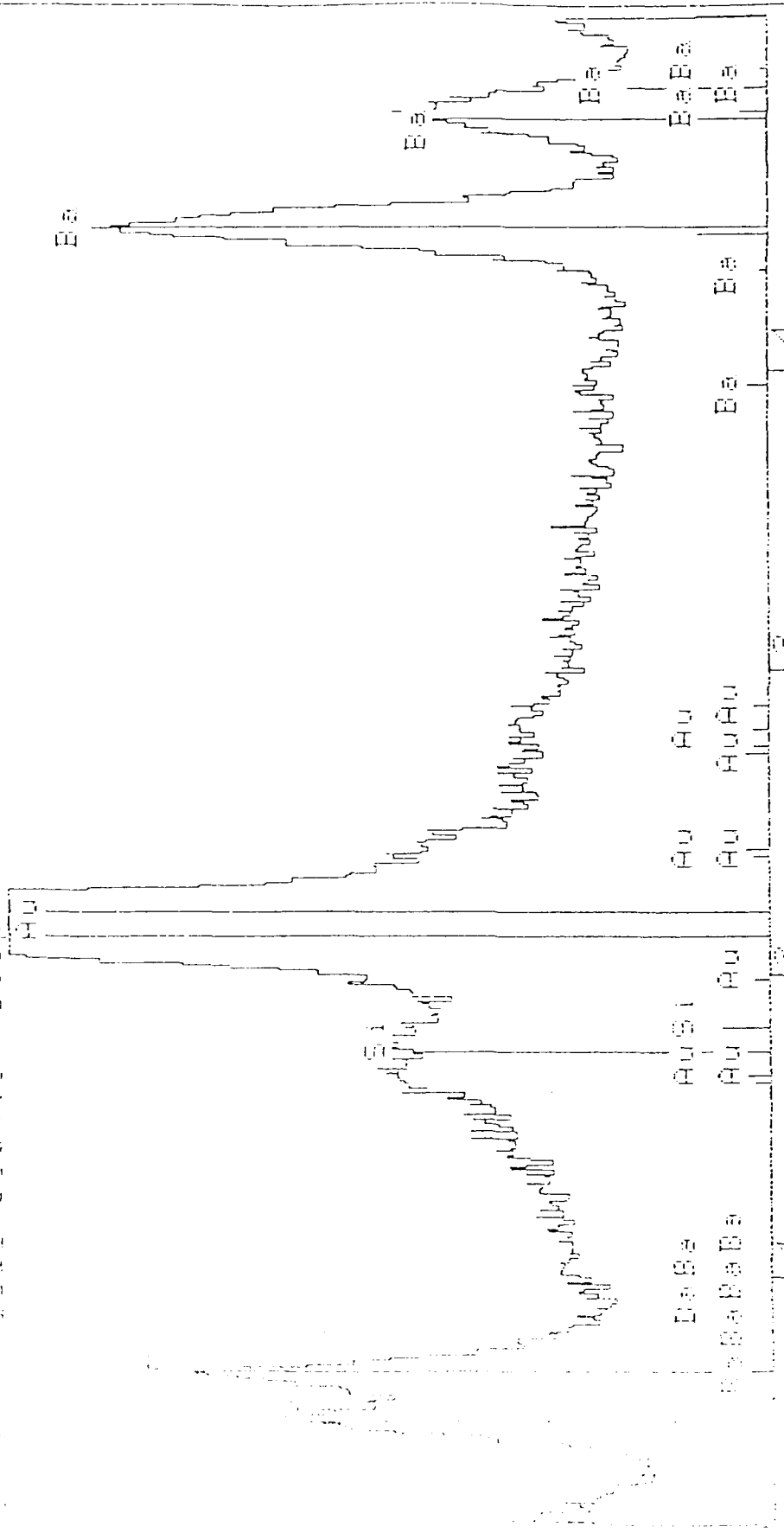
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1000 counts

35 sec



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235816

1000000

Table I - GARDINER et. al.

(a) Crystal Parameters

	1	2	3
formula	$C_{20}H_{24}F_{12}O_9Ba$	$C_{20}H_{20}F_6O_9Ba$	$C_{32}H_{60}O_9Ba$
space group	$\bar{P}1$	$\bar{P}1$	$\bar{P}1$
crystal system	triclinic	triclinic	triclinic
a , Å	9.6477(21)	9.5655(26)	10.6063(26)
b , Å	11.1547(22)	10.4002(29)	14.452(3)
c , Å	15.4645(31)	15.230(4)	15.463(4)
α , deg	94.151(16)	93.010(22)	115.311(18)
β , deg	90.730(17)	91.702(22)	97.739(20)
γ , deg	114.458(15)	109.631(21)	105.155(18)
V , Å ³	1509.2(5)	1423.3(6)	1984.0(8)
Z	2	2	2
cryst. dims., mm	0.38 x 0.40 x 0.42	0.38 x 0.38 x 0.40	0.45 x 0.22 x 0.
cryst color	colorless	colorless	colorless
$D(\text{calc})$, g/cm ³	1.702	1.553	1.215
$\mu(\text{MoK}\alpha)$, cm ⁻¹	14.61	15.07	10.61
temp, °C	23(1)	23(1)	23(1)
T(max)/T(min)	1.085	1.099	1.013

(b) Data Collection

diffractometer	Nicolet R3m
monochromator	graphite
scan technique	Wyckoff
radiation	MoK α (λ = 0.71073 Å)

(Continued)

Table 1. (Continued)

2 θ scan range, deg	4-50	4-57	4-48
data collected (h,k,l)	$\pm 12, \pm 14, \pm 19$	$\pm 13, \pm 14, \pm 21$	$\pm 13, \pm 17, \pm 18$
scan speed, deg/min	var. 5-20	var. 5-20	var. 10-30
rflns. collected	5539	7476	6477
indpt. rflns.	5320	7216	6217
$R(\text{merg}), \%$	1.95	2.49	2.64
indpt. rflns. obsvd. $F_o > 5\sigma(F_o)$	4207	5860	4909
std. rflns.	3 std/197 rflns	3 std/197 rflns	3std/197 rflns
var. in stds., %	<1	~2	<1

(c) Refinement

$R(F), \%$	4.85	4.30	4.63
$R(wF), \%$	5.34	4.64	4.85
$\Delta/\sigma(\text{max})$	0.086	0.006	0.056
$\Delta(\rho), e\text{\AA}^{-3}$	0.635	1.321	1.063
N_o/N_v	11.10	18.03	12.52
GOF	1.415	1.273	1.180

Table II - GARDINER et. al.

1		2		3	
Ba-O(1)	2.699(4)	Ba-O(6)	2.689(3)	Ba-O(4)	2.682(6)
Ba-O(2)	2.718(6)	Ba-O(7)	2.695(4)	Ba-O(3)	2.664(4)
Ba-O(3)	2.703(8)	Ba-O(8)	2.717(3)	Ba-O(1)	2.718(4)
Ba-O(4)	2.698(4)	Ba-O(9)	2.662(3)	Ba-O(2)	2.668(4)
Ba-O(6)	2.860(6)	Ba-O(1)	2.863(4)	Ba-O(5)	2.860(5)
Ba-O(7)	2.834(11)	Ba-O(2)	2.883(3)	Ba-O(6)	2.891(5)
Ba-O(8)	2.844(8)	Ba-O(3)	2.866(4)	Ba-O(7)	2.940(6)
Ba-O(9)	2.826(6)	Ba-O(4)	2.870(7)	Ba-O(8)	2.911(5)
Ba-O(5)	2.821(7)	Ba-O(5)	2.851(4)	Ba-O(9)	2.863(5)
O(1)-C(2)	1.224(9)	O(6)-C(2)	1.242(9)	O(4)-C(16)	1.244(9)
C(2)-C(3)	1.382(14)	C(2)-C(3)	1.386(9)	C(16)-C(17)	1.400(9)
C(3)-C(4)	1.345(10)	C(3)-C(4)	1.378(7)	C(17)-C(18)	1.388(11)
C(4)-O(2)	1.233(6)	C(4)-O(7)	1.237(6)	C(18)-O(3)	1.250(9)
C(2)-C(1)	1.550(11)	C(2)-C(1)	1.523(8)	C(16)-C(15)	1.541(12)
C(4)-C(5)	1.532(16)	C(4)-C(5)	1.524(11)	C(18)-C(19)	1.538(9)
O(3)-C(7)	1.229(7)	O(8)-C(7)	1.224(5)	O(1)-C(7)	1.241(6)
C(7)-C(8)	1.385(12)	C(7)-C(8)	1.411(8)	C(7)-C(6)	1.407(6)
C(8)-C(9)	1.387(13)	C(8)-C(9)	1.364(8)	C(6)-C(5)	1.403(8)
C(9)-O(4)	1.252(7)	C(9)-O(9)	1.258(5)	C(5)-O(2)	1.245(6)
C(7)-C(6)	1.490(15)	C(7)-C(6)	1.515(9)	C(7)-C(8)	1.536(8)
C(9)-C(10)	1.521(11)	C(9)-C(10)	1.518(7)	C(5)-C(4)	1.547(10)

TABLE III - GARAND *et al.*

1		2		3	
O(1)-Ba-O(2)	63.7(1)	O(6)-Ba-O(7)	64.3(1)	O(4)-Ba-O(3)	64.50(1)
O(1)-Ba-O(3)	144.8(2)	O(6)-Ba-O(8)	144.0(1)	O(4)-Ba-O(1)	144.1(1)
O(1)-Ba-O(4)	149.2(2)	O(6)-Ba-O(9)	147.9(1)	O(4)-Ba-O(2)	142.7(2)
O(1)-Ba-O(6)	106.4(1)	O(6)-Ba-O(1)	81.1(1)	O(4)-Ba-O(5)	116.3(1)
O(1)-Ba-O(7)	93.0(2)	O(6)-Ba-O(2)	75.4(1)	O(4)-Ba-O(6)	83.9(2)
O(1)-Ba-O(8)	74.0(2)	O(6)-Ba-O(3)	74.2(1)	O(4)-Ba-O(7)	72.0(2)
O(1)-Ba-O(9)	74.0(2)	O(6)-Ba-O(4)	92.5(1)	O(4)-Ba-O(8)	73.6(2)
O(1)-Ba-O(5)	85.4(2)	O(6)-Ba-O(5)	108.6(1)	O(4)-Ba-O(9)	76.4(2)
O(2)-Ba-O(3)	151.2(1)	O(7)-Ba-O(8)	151.2(1)	O(3)-Ba-O(1)	153.3(1)
O(2)-Ba-O(4)	89.5(1)	O(7)-Ba-O(9)	88.7(1)	O(3)-Ba-O(2)	90.0(1)
O(2)-Ba-O(6)	69.7(2)	O(7)-Ba-O(1)	71.6(1)	O(3)-Ba-O(5)	70.0(2)
O(2)-Ba-O(7)	111.5(2)	O(7)-Ba-O(2)	118.7(1)	O(3)-Ba-O(6)	93.6(2)
O(2)-Ba-O(8)	135.7(2)	O(7)-Ba-O(3)	136.9(1)	O(3)-Ba-O(7)	129.4(2)
O(2)-Ba-O(9)	115.8(2)	O(7)-Ba-O(4)	111.6(1)	O(3)-Ba-O(8)	127.4(2)
O(2)-Ba-O(5)	73.1(2)	O(7)-Ba-O(5)	70.9(1)	O(3)-Ba-O(9)	81.7(1)
O(3)-Ba-O(4)	63.9(2)	O(8)-Ba-O(9)	64.6(1)	O(1)-Ba-O(2)	63.7(1)
O(3)-Ba-O(6)	91.8(2)	O(8)-Ba-O(1)	108.0(1)	O(1)-Ba-O(5)	97.4(1)
O(3)-Ba-O(7)	72.0(2)	O(8)-Ba-O(2)	86.7(1)	O(1)-Ba-O(6)	98.7(2)
O(3)-Ba-O(8)	71.2(2)	O(8)-Ba-O(3)	70.4(1)	O(1)-Ba-O(7)	76.7(2)
O(3)-Ba-O(9)	84.6(2)	O(8)-Ba-O(4)	73.0(1)	O(1)-Ba-O(8)	68.7(2)
O(3)-Ba-O(5)	106.1(2)	O(8)-Ba-O(5)	91.4(1)	O(1)-Ba-O(9)	93.8(1)
O(4)-Ba-O(6)	75.4(2)	O(9)-Ba-O(1)	73.2(1)	O(2)-Ba-O(5)	76.1(1)

(Continu

Table III. (Continued)

1		2		3	
O(4)-Ba-O(7)	111.8(2)	O(9)-Ba-O(2)	105.1(1)	O(2)-Ba-O(6)	127.6(2)
O(4)-Ba-O(8)	134.7(2)	O(9)-Ba-O(3)	134.4(1)	O(2)-Ba-O(7)	140.4(2)
O(4)-Ba-O(9)	107.8(2)	O(9)-Ba-O(4)	113.8(1)	O(2)-Ba-O(8)	105.7(1)
O(4)-Ba-O(5)	71.7(2)	O(9)-Ba-O(5)	76.6(1)	O(2)-Ba-O(9)	72.1(2)
Ba-O(1)-C(2)	136.1(5)	Ba-O(6)-C(2)	137.5(3)	Ba-O(4)-C(16)	139.0(4)
O(1)-C(2)-C(1)	111.5(8)	O(6)-C(2)-C(1)	115.9(6)	O(4)-C(16)-C(15)	115.7(6)
O(1)-C(2)-C(3)	128.0(6)	O(6)-C(2)-C(3)	125.7(4)	O(4)-C(16)-C(17)	125.0(7)
C(2)-C(3)-C(4)	124.0(7)	C(2)-C(3)-C(4)	124.6(5)	C(16)-C(17)-C(18)	126.8(7)
C(1)-C(2)-C(3)	120.5(7)	C(1)-C(2)-C(3)	118.4(5)	C(15)-C(16)-C(17)	119.3(7)
C(3)-C(4)-O(2)	129.1(9)	C(3)-C(4)-O(7)	129.9(6)	C(17)-C(18)-O(3)	124.9(5)
C(3)-C(4)-C(5)	119.2(7)	C(3)-C(4)-C(5)	116.1(5)	C(17)-C(18)-C(19)	119.9(7)
C(5)-C(4)-O(2)	111.6(6)	C(5)-C(4)-O(7)	114.0(4)	C(19)-C(18)-O(3)	115.1(7)
C(4)-O(7)-Ba	135.9(5)	C(4)-O(7)-Ba	134.5(3)	C(18)-O(3)-Ba	139.6(4)
Ba-O(3)-C(7)	136.9(6)	Ba-O(8)-C(7)	137.3(4)	Ba-O(1)-C(7)	134.9(4)
O(3)-C(7)-C(6)	115.7(8)	O(8)-C(7)-C(6)	118.1(5)	O(1)-C(7)-C(8)	117.3(5)
O(3)-C(7)-C(8)	127.5(8)	O(8)-C(7)-C(8)	124.0(5)	O(1)-C(7)-C(6)	124.2(5)
C(6)-C(7)-C(8)	116.8(6)	C(6)-C(7)-C(8)	117.9(4)	C(8)-C(7)-C(6)	118.5(4)
C(7)-C(8)-C(9)	123.5(6)	C(7)-C(8)-C(9)	125.6(4)	C(7)-C(6)-C(5)	126.8(5)
C(8)-C(9)-C(10)	117.1(6)	C(8)-C(9)-C(10)	118.7(4)	C(6)-C(5)-C(4)	119.4(5)
C(8)-C(9)-O(4)	128.2(7)	C(8)-C(9)-O(9)	129.1(4)	C(6)-C(5)-O(2)	124.2(5)
C(10)-C(9)-O(4)	114.7(7)	C(10)-C(9)-O(9)	112.3(5)	C(4)-C(5)-O(2)	116.3(5)
C(9)-O(4)-Ba	136.5(5)	C(9)-O(9)-Ba	134.8(3)	C(5)-O(2)-Ba	135.0(4)

Supplementary Material

Table A. Atomic coordinates ($\times 10^4$) and isotropic thermal parameters ($\text{\AA}^2 \times 10^3$) for $\text{BaC}_{20}\text{H}_{24}\text{F}_{12}\text{O}_9$ (1).

Table B. Atomic coordinates ($\times 10^4$) and isotropic thermal parameters ($\text{\AA}^2 \times 10^3$) for $\text{BaC}_{20}\text{H}_{30}\text{F}_6\text{O}_9$ (2).

Table C. Atomic coordinates ($\times 10^4$) and isotropic thermal parameters ($\text{\AA}^2 \times 10^3$) for $\text{BaC}_{20}\text{H}_{60}\text{O}_9$ (3).

	x	y	z	U*
Ba	4517.5(4)	5003.1(3)	2539.6(2)	66.0(2)
O(1)	6447(5)	7414(4)	3252(3)	93(2)
O(2)	3212(5)	6541(4)	3283(3)	94(2)
O(3)	4317(6)	2683(4)	1764(3)	95(2)
O(4)	1820(5)	3432(4)	1717(3)	95(2)
O(5)	3960(8)	6375(6)	1212(4)	126(3)
O(6)	2610(8)	3700(6)	3890(4)	140(3)
O(7)	5383(11)	3676(10)	3792(5)	169(6)
O(8)	7440(7)	4956(8)	2644(6)	158(4)
O(9)	6527(7)	6150(8)	1263(4)	150(4)
F(1)	8789(8)	9695(6)	2944(4)	201(4)
F(2)	8679(8)	9631(7)	4260(5)	221(5)
F(3)	7840(10)	10784(6)	3636(6)	222(5)
F(4)	1359(9)	7788(9)	3128(5)	222(6)
F(5)	2727(10)	9328(7)	3971(6)	230(6)
F(6)	1601(10)	7434(8)	4390(5)	226(6)
F(7)	4448(11)	350(6)	2028(4)	219(6)
F(8)	4376(15)	463(9)	726(5)	321(10)
F(9)	2671(12)	-667(6)	1295(7)	275(7)
F(10)	-1228(7)	555(6)	892(5)	196(4)
F(11)	-1236(6)	2114(8)	1668(5)	191(4)
F(12)	-570(7)	2478(8)	467(4)	238(5)
C(1)	7970(13)	9623(8)	3582(5)	134(5)
C(2)	6367(8)	8461(6)	3464(4)	84(3)
C(3)	5076(11)	8673(7)	3623(4)	107(4)
C(4)	3651(9)	7715(6)	3546(4)	88(3)
C(5)	2309(12)	8070(9)	3751(6)	129(5)
C(6)	3764(15)	491(8)	1379(5)	134(6)
C(7)	3295(9)	1605(6)	1511(4)	85(3)
C(8)	1776(10)	1317(6)	1328(4)	95(4)
C(9)	1173(8)	2250(6)	1414(4)	81(3)
C(10)	-470(10)	1817(9)	1085(6)	118(4)
C(11)	1106(11)	3600(11)	3879(7)	162(6)
C(12)	2860(18)	2865(11)	4314(7)	203(10)
C(13)	4408(20)	3025(14)	4373(10)	222(12)
C(14)	6747(19)	3782(19)	3895(10)	251(14)
C(15)	7498(16)	3917(15)	3143(8)	230(11)
C(16)	8148(13)	5285(15)	1827(9)	240(11)
C(17)	8195(18)	6384(15)	1513(14)	260(12)
C(18)	6512(16)	7162(12)	891(10)	217(9)
C(19)	5019(16)	6859(12)	592(7)	186(9)
C(20)	2448(12)	6259(10)	1029(6)	146(7)

* Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor

TABLE A - GARDINER et al.

	x	y	z	U*
Ba	639.2(2)	41.0(2)	2448.6(1)	54.4(1)
O(1)	1351(4)	-1500(4)	3789(2)	86(1)
O(2)	-1361(4)	-1113(4)	3803(2)	84(1)
O(3)	-2386(4)	-38(4)	2346(3)	96(2)
O(4)	-506(6)	1351(7)	1132(3)	142(3)
O(5)	2339(5)	1507(5)	1088(3)	127(2)
O(6)	-967(4)	-2491(3)	1784(2)	87(1)
O(7)	2227(4)	-1420(3)	1739(2)	83(1)
O(8)	456(4)	2381(3)	3235(2)	82(1)
O(9)	3115(4)	1676(3)	3306(3)	89(1)
F(1)	3209(7)	-4127(6)	939(5)	258(5)
F(2)	4143(8)	-2909(9)	2001(5)	250(5)
F(3)	4218(8)	-2154(8)	846(5)	255(5)
F(4)	6035(5)	3085(6)	3252(4)	181(3)
F(5)	5503(5)	2898(7)	4563(4)	214(4)
F(6)	5883(5)	4740(4)	3970(4)	179(3)
C(1)	-2129(9)	-4847(6)	1439(5)	139(4)
C(2)	-748(6)	-3575(4)	1573(3)	84(2)
C(3)	623(7)	-3706(4)	1427(3)	88(2)
C(4)	1961(6)	-2645(5)	1520(3)	77(2)
C(5)	2337(9)	-3013(7)	1321(5)	114(3)
C(6)	569(8)	4645(6)	3675(4)	108(3)
C(7)	1312(6)	3517(4)	3488(3)	72(2)
C(8)	2855(6)	3830(4)	3645(3)	77(2)
C(9)	3500(5)	2920(4)	3571(3)	72(2)
C(10)	5246(6)	3409(6)	3836(4)	97(2)
C(11)	2879(7)	-1235(7)	4010(4)	121(3)
C(12)	509(7)	-1765(5)	4522(3)	92(2)
C(13)	-1069(8)	-2203(7)	4229(5)	114(3)
C(14)	-2889(6)	-1391(7)	3563(5)	122(3)
C(15)	-3099(6)	-218(8)	3160(5)	127(3)
C(16)	-2685(8)	954(7)	1889(4)	126(4)
C(17)	-2036(9)	997(9)	1029(5)	149(5)
C(18)	311(10)	1963(9)	494(6)	167(6)
C(19)	1858(10)	2382(7)	630(5)	136(4)
C(20)	3854(8)	1755(8)	1157(5)	158(4)

* Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor

TABLE B- GARDINER et al

	x	y	z	U
Ba	1559.3(3)	4490.8(3)	1932.1(3)	53.5(2)
O(1)	3101(4)	6461(3)	2182(3)	64(2)*
O(2)	618(4)	6120(3)	2710(3)	70(2)*
O(3)	-700(4)	3098(4)	1882(4)	81(3)*
O(4)	1846(4)	2783(4)	2105(4)	88(3)*
O(5)	-653(5)	3991(4)	331(3)	93(3)*
O(6)	1336(6)	3151(5)	-145(4)	115(4)*
O(7)	3866(5)	4056(4)	1189(4)	117(4)*
O(8)	4291(4)	5275(5)	3228(4)	112(4)*
O(9)	2080(5)	5234(4)	4028(3)	101(3)*
C(1)	-1099(12)	6950(12)	3567(14)	266(14)*
C(1')	-867(26)	7663(20)	3306(19)	67(7)
C(2)	477(18)	8791(13)	4077(14)	242(17)*
C(2')	1078(25)	8771(21)	4783(18)	66(7)
C(3)	1027(16)	7960(17)	5016(10)	246(18)*
C(3')	-214(29)	6836(24)	4384(21)	82(9)
C(4)	316(7)	7659(5)	3960(5)	84(4)*
C(5)	1149(5)	7126(4)	3280(4)	56(3)*
C(6)	2415(6)	7785(4)	3322(4)	65(3)*
C(7)	3315(5)	7431(4)	2779(4)	54(3)*
C(8)	4664(5)	8291(5)	2942(5)	68(3)*
C(9)	5183(9)	7881(7)	2046(7)	142(6)*
C(10)	5663(7)	8434(8)	3821(7)	135(6)*
C(11)	4574(8)	9382(6)	3175(8)	133(7)*
C(12)	3150(11)	1951(10)	3085(12)	245(13)*
C(13)	2272(18)	712(14)	1424(11)	325(17)*
C(14)	1189(11)	451(10)	2543(11)	230(14)*
C(15)	1903(7)	1247(5)	2282(7)	97(5)*
C(16)	1136(6)	1951(5)	2109(5)	73(3)*
C(17)	-266(6)	1645(5)	2002(5)	79(4)*
C(18)	-1100(5)	2202(5)	1879(4)	66(3)*
C(19)	2622(6)	1759(6)	1795(6)	86(4)*
C(20)	-3120(9)	661(10)	1716(12)	214(13)*
C(21)	-3450(8)	1684(8)	884(7)	134(7)*
C(22)	-2894(9)	2543(12)	2668(8)	241(11)*
C(23)	-1748(7)	4337(7)	518(6)	106(5)*
C(24)	-940(9)	3063(7)	-564(6)	107(5)*
C(25)	152(11)	2779(9)	-794(8)	176(7)*
C(26)	2411(11)	2840(9)	-393(8)	169(8)*
C(27)	3577(12)	3306(14)	276(8)	299(15)*
C(28)	5108(10)	4599(14)	1888(9)	224(13)*
C(29)	5248(9)	4996(10)	2830(10)	151(8)*
C(30)	4432(8)	5708(9)	4205(7)	148(7)*
C(31)	3415(10)	5861(11)	4582(7)	186(9)*
C(32)	1407(11)	4584(8)	4347(7)	153(7)*

* Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor

TABLE C - GARDINER et al.