An accuracy assessment of the refinement of partial metal disorder in solid solutions of Al(acac)$_3$ and Cr(acac)$_3$

Simon G. Bott,[*a] **Bradley D. Fahlman,**[b] **Milton L. Pierson**[c] **and Andrew R. Barron**[*b]

[a] *Department of Chemistry, University of Houston, Houston, Texas 77204, USA.*
E-mail: sbott@Bayou.uh.edu
[b] *Department of Chemistry and Center for Nanoscale Science and Technology, Rice University,*
Houston, Texas 77005, USA. E-mail: arb@rice.edu
[c] *Department of Geology and Geophysics, Rice University, Houston, Texas 77005, USA*

A series of solid solutions have been prepared by co-crystallization of Al(acac)$_3$ and Cr(acac)$_3$ and studied by X-ray diffraction. The end members and seven isotopic members of the series Al$_{1-x}$Cr$_x$(acac)$_3$, with x varying from 0.02 to 0.91, crystallize in the monoclinic space group $P2_1/c$ with $Z = 4$. The unit cell parameters vary slightly with composition, and fall into the following ranges: a, 13.987–14.009; b, 7.534–7.553; c, 16.308–16.348 Å; β, 98.78–98.99°. The cell axes do not vary in a linear manner with the mole% Cr. The Al : Cr molar ratio in each crystal studied by X-ray diffraction was determined by wavelength dispersive spectroscopy (WDS) and compared with the refinement of the Al : Cr site occupancy, which was attempted by the following methods: (1) refinement based upon bulk sample analysis, (2) refinement of occupancy with common displacement parameters, (3) refinement of occupancy and displacement parameters, and (4) construction of a mixed atom type based on the results of all three methods. Results from methods 2 and 3 were found to agree with WDS data within experimental error for all crystals studied. Method 1 was the least successful, the refinement often being significantly problematic. A discussion of suitable methods for refinement of partial site occupancy in solid solutions for isomorphous structures is presented. The variance of crystal lattice parameters and the M–O and O–M–O structural parameters with Al : Cr ratio is investigated.

Introduction

Metal β-diketonates serve as non-toxic, volatile and inexpensive precursors for the chemical vapor deposition (CVD) of metal and metal oxide thin films.[1–3] They are relatively easy to synthesize and are chemically and thermally stable in the region bordered by the evaporation and transport temperatures, even after prolonged use. These properties account for the continued utilization of these complexes in CVD processes.[4–9] Recently, there has been interest in obtaining thin films of mixed metal oxides for applications such as mixed-metal dielectrics or high-T_c superconducting films. One method involves CVD using multiple metal β-diketonate precursors. One alternative method that we have recently investigated is to use single crystals consisting of mixed metal β-diketonate compounds as MOCVD precursors. Through the utilization of such precursors, one should be able to control the metal stoichiometry in the resultant film by modifying the composition of the precursor crystal.

Metal β-diketonate complexes are isostructural and often isomorphous. Thus, crystals obtained from co-crystallization of two or more metal β-diketonate complexes may be thought of as a hybrid of the precursors; that is, the metal position in the crystal lattice may be defined as having the average metal composition.

Crystallographic positional disorder is evident when a position in the lattice is occupied by two or more atoms, the average of which constitutes the bulk composition of the crystal. If a particular atom occupies a certain position in one unit cell and another atom occupies the same position in other unit cells, the resulting electron density will be a weight average of the situation in all the unit cells throughout the crystal. Since the diffraction experiment involves the average of a very large number of unit cells (of the order of 10^{18} in a crystal used for X-ray diffraction analysis), minor static displacements of atoms closely simulate the effects of vibrations on the scattering power of the "average" atom. However, the determination of the "average" atom in a crystal may be complicated if positional disorder is encountered. As many crystallographers have noted, one should always be cautious when utilizing crystallography to determine the absolute composition of desired compounds. Crystal disorder involving groups such as CO, CN and Cl has been documented to create problems in assigning the correct structure through refinement procedures.[10,11] One of the most comprehensive studies of crystallographic disorder was carried out by Cotton and co-workers on a series of solid solutions of Jahn–Teller compounds in undistorted hosts.[12–15] In this study, atomic absorption analyses were carried out on the material from which crystals were grown. This assumes that (a) the crystal on which X-ray data collection was performed is representative of the bulk material, and (b) the composition of the solid solution is uniform throughout the individual crystal. Thus, while attempts have been made to correlate crystallographic lattice parameters with the bulk chemical composition of the acetone solution from which the single crystal was grown, there has been little effort to correlate crystallographic site occupancy with the chemical composition of the crystal from which single crystal diffraction data were obtained. These are two very different issues. The first is aimed at determining the relationship of a single crystal to the bulk material. The second, is aimed at determining if refinement of a site-occupancy factor actually gives a realistic value for % occupancy when compared to the "actual" % composition for that particular single crystal.

As part of our general studies we undertook an X-ray diffraction study of a crystal obtained from a sample containing an Al : Cr ratio of 60 : 40. However, the structural refinement

Table 1 Comparison of lattice parameters for Al(acac)₃ and Cr(acac)₃

	Al(acac)₃			Cr(acac)₃	
	lit.[a]	lit.[b]	this work	lit.[c]	this work
a/Å	14.069(9)	13.972(3)	13.941(2)	14.031	13.989(3)
b/Å	7.568(5)	7.527(2)	7.514(1)	7.551	7.534(1)
c/Å	16.37(1)	16.307(5)	16.265(3)	16.379	16.329(3)
β/°	99(5)	98.88(2)	98.81(3)	99.06	98.97(3)

[a] Ref. 18. [b] Ref. 19. [c] Ref. 20.

Table 2 Variance in chromium concentrations (%) for samples of Al₁₋ₓCrₓ(acac)₃

Sample	Bulk (% Cr)	WDS (% Cr)	X-Ray diffraction (% Cr)
1	13	1.9 ± 0.2	0[a]
2	2	2.1 ± 0.3	0[a]
3	20	17.8 ± 1.6	17.3 ± 1.8
4	26	26.7 ± 1.7	28.3 ± 1.9
5	18	48.5 ± 4.9	46.7 ± 2.1
6	60	75.1 ± 4.1	72.9 ± 2.4
7	80	91.3 ± 1.2	82.3 ± 3.1

[a] Concentration was too low successfully to refine the chromium occupancy.

suggested that the Al : Cr ratio was in fact significantly higher.[16] A wavelength dispersive spectroscopy (WDS) study of the crystals upon which X-ray diffraction data were collected revealed that the Al : Cr ratio in individual crystals was not representative of the bulk material.

Given these observations, we set out to quantitatively assess the accuracy of methods utilized to determined crystal structures of disordered compounds. The positional disorder in strontium barium niobate was recently studied by Trubelja *et al.* in which they utilized Rietveld structure refinement (based on powder X-ray diffraction data) to determine which lattice sites the metals occupied in the structure.[17] However, there have been few other reports of studies that quantitatively assess the accuracy of methods utilized to describe structures of positionally disordered compounds with respect to the "actual" composition of the crystal from which X-ray diffraction data were obtained. Herein we report our study dealing with the effectiveness of crystallography in modeling the partial occupancy of the disordered metals in mixed, solid solution, Al₁₋ₓCrₓ(acac)₃ crystals containing various metal ratios.

Results and discussion

Table 1 provides a comparison of the crystal and lattice parameters for Al(acac)₃ and Cr(acac)₃ obtained from the literature[18–20] and in our laboratory. The isomorphous nature of these structures makes their solid solutions suitable for a quantitative investigation of possible routes to accurate modeling of site disorder.

Crystals of the solid solutions Al₁₋ₓCrₓ(acac)₃ suitable for X-ray crystallography were formed by the crystallization from acetone solutions of specific mixtures of Al(acac)₃ and Cr(acac)₃, see Experimental section. Table 2 summarizes the percentage of chromium present in the bulk material for samples **1**–**7**. X-Ray diffraction data were collected on a crystal from each sample, and the molecular structure was determined. Substitution of Cr for Al in the M(acac)₃ structure could possibly occur in a random manner, *i.e.* a metal site has an equal probability of containing an aluminium or a chromium atom. Alternatively, if the chromium had preference for specific sites a superlattice structure of lower symmetry would be present. Such an ordering is not observed since all the samples show
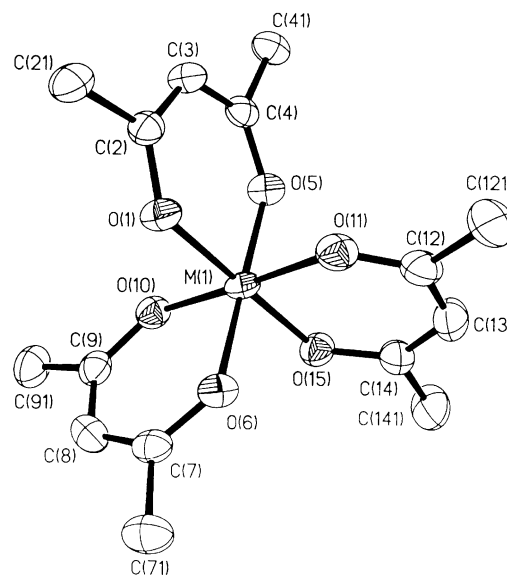
Fig. 1 Molecular structure of Al₁₋ₓCrₓ(acac)₃. Thermal ellipsoids are shown at the 30% level and hydrogen atoms are omitted for clarity.
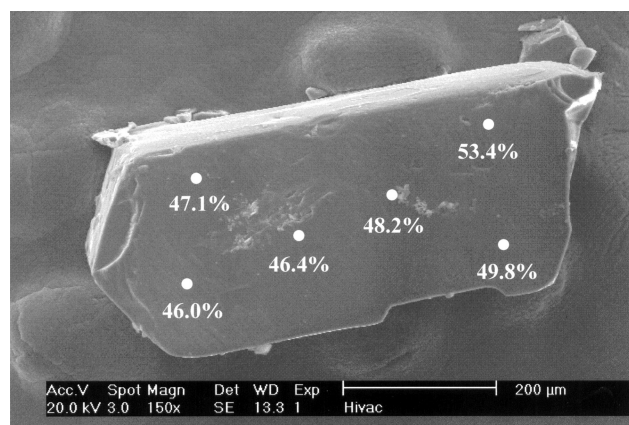
Fig. 2 SEM image of a representative crystal used for WDS and X-ray diffraction analysis showing the location and results for the WDS analysis. The 10 μm sized analysis spots are represented by the white dots.

no additional reflections other than those that may be indexed to the monoclinic cell. Therefore, it may be concluded that the Al(acac)₃ and Cr(acac)₃ do indeed form solid solutions: Al₁₋ₓCrₓ(acac)₃. A representative example of the structure of Al₁₋ₓCrₓ(acac)₃ is shown in Fig. 1.

Electron microprobe analysis was performed on the individual crystals from which X-ray crystallographic data were collected. Analysis was performed on at least 6 sites on each crystal using a 10 μm sized analysis spot providing a measure of the homogeneity within the individual crystal. An example of an SEM image of one of the crystals and the point analyses is given in Fig. 2. The data in Table 2 and Fig. 2 demonstrate that while a batch of crystals may contain individual crystals with different compositions, each individual crystal is actually reasonably homogeneous.

As may be seen from Table 2, there is, for most samples, a significant variance between the molar Al : Cr ratio in the bulk material and an individual crystal chosen for X-ray diffraction. We have previously observed a similar, but smaller, variance between bulk and crystalline phases for CuInS₂₋ₓSeₓ and CuInSe₂₋ₓTeₓ solid solutions.[21] The variation in Al : Cr ratio within each individual crystal there is much less than between crystals. As may be seen from Table 2, the variation is generally ±10%. It should be noted that under the conditions employed in this study microprobe analysis has an analysis depth of 2–3 μm, which limits the volume of sample analyzed. This

result highlights the anomaly often observed between bulk composition and a crystal structure determination.

X-Ray diffraction determination of Al : Cr ratio

In an attempt to find the optimal approach for the determination of metal concentration in solid solutions a range of methods were used to refine the crystal structures. An atom in a structure is defined by several parameters: the type of atom, the positional coordinates (x, y, z), the occupancy factor (how many "atoms" are at that position) and atomic displacement parameters (often called temperature or thermal parameters).[22] The latter can be thought of as being a "picture" of the volume occupied by the atom over all the unit cells, and can be isotropic (1 parameter defining a spherical volume) or anisotropic (6 parameters defining an ellipsoidal volume). For a "normal" atom the occupancy factor is fixed as being equal to one, and the positions and displacement parameters are "refined" using least-squares methods to values in which the best agreement with the observed data is obtained. In crystals with site disorder one position is occupied by different atoms in different unit cells. This refinement requires a more complicated approach. Two broad methods may be used: either a new atom type that is the appropriate combination of the different atoms is defined, or the same positional parameters are used for different atoms in the model, each of which has occupancy values less than one, and for which the sum is constrained to total one. In both approaches the relative occupancies of the two atoms are required. For the first approach these occupancies have to be defined. For the second the value can be refined. However, there is a relationship between the thermal parameter and the occupancy value so care must be taken when doing this. In order to determine the best method these issues were addressed in several ways.

Method 1. A very simplistic assumption that the crystals would represent the bulk sample was made for each structure. Either a new atom type was generated that was the appropriate combination of the measured percent composition of Al and Cr or two different atoms were input with the occupancy factor set to reflect the percent composition. The thermal parameters were allowed to refine as usual. In all cases, structure refinement converged, but the quality of refinement varied.

Since Method 1 does not refine the % Cr and relies on an input for the percent composition of Al and Cr of the "bulk" material (*i.e.* the % Cr in the total mass of the material as opposed to the analysis of the single crystal on which X-ray diffraction was performed, see Table 2, Column 2), the closer these values were to the "actual" value determined by WDS for the crystal on which X-ray diffraction was performed (see Table 2, Column 3) then the closer the overall refinement of the structure to those of Methods 2–4. Thus, as may be seen from Table 2, the % Cr in the bulk material in sample **5** is 18% while the value analyzed for the crystal on which X-ray diffraction data was collected is 48.5%. Thus, use of a fixed (unrefined) % Cr of 18%, for the structure solution of sample **5**, will not result in a good refinement of the overall structure.

While this assumption is obviously invalid for many of the structures (*i.e.* sample **1** and **5**, see Table 2), it is one often used when bulk data (for example, from NMR) are available. However, as there is never any reason to assume that one crystal is completely representative of the bulk sample, it is unwise to rely only on such data.

Method 2. The occupancy values were refined (such that their sum was equal to 1) while the two atoms were constrained to have the same displacement parameters. This method always produced final, refined, occupancy values that were close to those obtained from WDS (Table 2). This approach assumes that the motion of the central metal atoms is identical. While
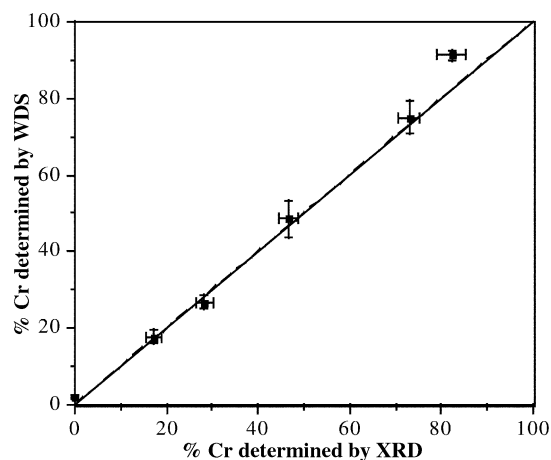

Fig. 3 Comparison of the chromium concentration determined from WDS (with error) and refinement of X-ray diffraction data (with error).

this is obviously not strictly true as they are of different size, the results obtained herein imply that this is a reasonable approximation where simple connectivity data are required. For both samples **1** and **2** the amount of Cr was so low that a good refinement could not be obtained. When refining the occupancy values, that for Al would exceed 1 while that of Cr would be less than 1. The best refinement in both cases was obtained assuming 100% aluminium.

Method 3. The occupancy values (such that their sum was equal to 1) and the displacement parameters were all refined. In some cases, despite the interrelationship between the two types of parameter, convergence was obtained successfully. This was the case for samples **3** and **4**, and the refined occupancies were both slightly closer to those observed from WDS than the occupancy values obtained using Method 2. However, when this approach was tried for samples **5** through **7** the refinement was unstable and would not converge. Whether this observation was due to the increased percentage of Cr or simply lower data quality than is the case for samples **3** and **4** is not certain. However, while this method does allow refinement of any differences in atomic motion between the two metals, it requires extremely high quality data for this difference to be determined reliably.

Method 4. Finally, once the best values for occupancy were obtained using either Method 2 or 3, these values were fixed and the displacement parameters were allowed to refine freely. This approach added little to the final results.

Fig. 3 shows the relationship between the chromium concentration (% Cr) determined from WDS and the refinement of X-ray diffraction data using method 2 (**1**, **2**, **5**–**7**) or 3 (**3** and **4**). Clearly there exists a good correlation, with only a slight divergence at high chromium concentration. This is undoubtedly a consequence of trying to refine a low fraction of a light atom (Al) in the presence of a large fraction of a heavier atom (Cr). We may conclude, therefore, that X-ray diffraction is an accurate method of determining the M : M' ratios in crystalline solid solution.

Lattice and structural parameter variation with Al : Cr ratio

It would be expected from a consideration of the relative ionic radii of Al^{3+} (0.51 Å [23]) and Cr^{3+} (0.63 Å) that the lattice parameters of the $Al_{1-x}Cr_x(acac)_3$ solid solution increase with increased chromium content. It should be noted that the literature values reported for the lattice parameters for $Al(acac)_3$ vary greatly, see Table 1.[18–20] In part this may be due to the measurement of the earliest data on film,[20] however in order to provide a better comparison with our data for the $Al_{1-x}Cr_x(acac)_3$ solid solution we have redetermined the structures of $Al(acac)_3$ solid and $Cr(acac)_3$ (see Table 1) and found the lattice

Table 3 Summary of X-ray diffraction data for solid solutions of $Al_{1-x}Cr_x(acac)_3$[a]

Sample	1	2	3	4	5	6	7
M_w	324.27	324.27	328.61	331.8	335.25	342.51	344.90
a/Å	14.002(3)	13.998(3)	14.009(3)	13.995(3)	13.987(3)	14.004(3)	14.007(3)
b/Å	7.534(2)	7.542(2)	7.552(2)	7.538(2)	7.553(2)	7.546(2)	7.544(2)
c/Å	16.326(3)	16.315(3)	16.332(3)	16.308(3)	16.333(3)	16.348(3)	16.344(3)
β/°	98.81(3)	98.78(3)	98.83(3)	98.85(3)	98.94(3)	98.96(3)	98.99(3)
V/Å³	1701.8(6)	1702.2(6)	1707.3(6)	1699.8(6)	1704.5(6)	1706.5(6)	1705.9(6)
μ/mm⁻¹	0.14	0.14	0.24	0.30	0.38	0.54	0.60
No. reflections collected	7823	7474	7369	7434	7811	7877	7900
No. independent reflections	2449	2450	2443	2446	2447	2460	2471
R_{int}	0.0381	0.0444	0.053	0.048	0.087	0.110	0.128
No. data observed[b]	1226	1241	1466	1560	1938	1167	1678
R	0.0725	0.1025	0.0551	0.0583	0.0633	0.0611	0.0642
R_w	0.1733	0.1992	0.1609	0.1501	0.1860	0.1617	0.1720

[a] Constant parameters for all samples: monoclinic, space group $P2_1/c$, $Z = 4$, $T = 298$ K. [b] Observed data criterion ($|F_o| > 4.0\sigma|F_o|$).
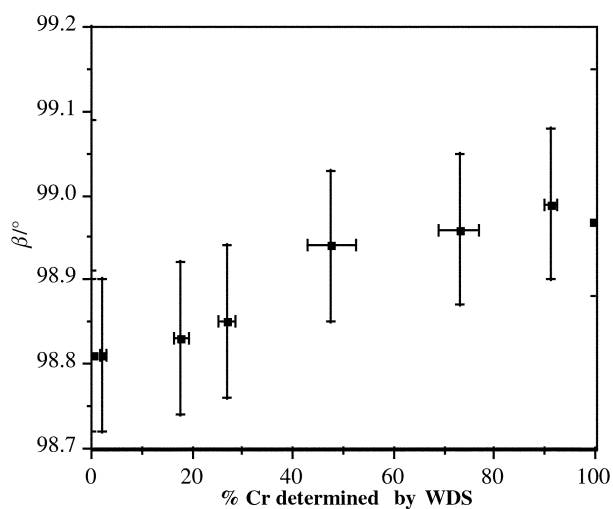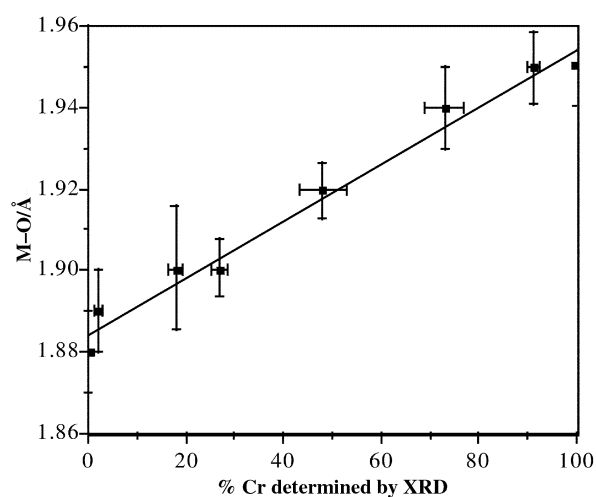

Fig. 4 Plot of the crystal lattice parameter β for $Al_{1-x}Cr_x(acac)_3$ as a function of the chromium concentration (% Cr) determined from WDS.

Fig. 5 Plot of the M–O distance, with esds, for $Al_{1-x}Cr_x(acac)_3$ as a function of the chromium concentration (% Cr) determined from WDS ($R = 0.985$).

parameters to follow the expected trend, *i.e.* the values for Cr < Al.

Vergard's law requires the lattice constant for a linear solution of two materials to vary linearly with composition, however a parabolic behavior is often observed.[24] The accuracy of the lattice parameter *versus* "concentration variable" (*x*) curves often allows for relative concentrations of constituents within the samples to be determined where the values are unknown from analysis. A consideration of the lattice constants *versus* chromium content (% Cr), see Table 3, shows that for the molecular species described herein no clear relationship is observed with the exception of the value for β, see below. In fact there appears to be essentially invariance in the lattice parameters (*a*, *b*, and *c*) within experimental error. The near linear correlation of β with % Cr as determined by WDS (Fig. 4) is surprising since this parameter is often considered flexible for isomorphous monoclinic cells, as compared to the lattice parameters, *a*, *b*, and *c*.

Based upon the forgoing, it appears that the lattice parameters for molecular materials cannot be used as an accurate measure of composition. This is in contrast to the well accepted situation for purely inorganic solid state materials. A likely explanation is that for molecular materials the lattice is obviously defined by the flexible organic "spinach" surrounding the metal core. Disorder within the core little effects the overall packing and hence the cell is defined by the ligands. The only exception to this will be disorder between different ligands.[4,5] Furthermore, it appears that the accuracy of the determination of the site disorder (*i.e.* % Cr) is independent of the cell constants relationship to the parent compounds.

The variance of structural parameters with Al : Cr ratio is essentially nil. As may be observed from Table 4, there is essentially no change in the various O–M–O bond angles across the composition of the solid solutions, although, as expected from the relative ionic radii, there is a slight increase in the M–O bond distance with increased chromium content, see Fig. 5.

Experimental

Acetone (99.9+%, HPLC grade), $Al(acac)_3$ and $Cr(acac)_3$ were obtained from Aldrich and used without further purification. The appropriate amounts of $Al(acac)_3$ and $Cr(acac)_3$ (*ca.* 2.0 g total) were dissolved in acetone (*ca.* 30 mL) and heated slightly. Any undissolved material was removed by filtration. Crystals suitable for X-ray crystallography were formed upon cooling (−25 °C) overnight. The color varied from light to dark purple depending on the chromium concentration.

Crystallographic studies

Crystals of samples **1**–**7**, $Al(acac)_3$ and $Cr(acac)_3$ were mounted on a glass fiber. Crystal and data collection and solution details for samples **1**–**7** are given in Table 3. Standard procedures in our laboratory have been described previously.[25] Data were collected on a Bruker CCD SMART system, equipped with graphite monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) and corrected for Lorentz and polarization effects. The structures were solved using the direct methods program XS[26] and Fourier difference maps and refined by using full matrix least squares methods.[27] Full details of the methods used are given in the Results and Discussion. All atoms were refined with anisotropic thermal parameters. All the hydrogen atoms were placed in calculated positions [$U_{iso} = 0.08$ Å²; $d(C–H) = 0.96$ Å] for

Table 4 Selected bond lengths (Å) and angles (deg) in $Al_{1-x}Cr_x(acac)_3$

	1[a]	3	4	5	6	7
M(1)–O(1)	1.890(3)	1.903(4)	1.902(2)	1.925(2)	1.937(3)	1.948(3)
M(1)–O(5)	1.888(3)	1.900(6)	1.902(2)	1.927(2)	1.943(4)	1.951(3)
M(1)–O(6)	1.877(3)	1.900(6)	1.907(2)	1.931(2)	1.946(4)	1.957(3)
M(1)–O(10)	1.881(3)	1.893(6)	1.903(3)	1.913(2)	1.934(4)	1.944(3)
M(1)–O(11)	1.873(4)	1.891(6)	1.893(3)	1.904(2)	1.927(4)	1.935(3)
M(1)–O(15)	1.878(3)	1.889(4)	1.893(2)	1.916(2)	1.940(4)	1.948(3)
O(1)–M(1)–O(5)	91.2(1)	91.3(2)	91.3(1)	91.33(9)	91.2(2)	91.3(1)
O(1)–M(1)–O(6)	90.0(1)	89.8(2)	89.9(1)	89.86(9)	89.9(1)	90.1(1)
O(1)–M(1)–O(10)	90.0(1)	89.8(2)	89.5(1)	89.3(1)	88.8(2)	88.9(1)
O(1)–M(1)–O(11)	88.0(2)	88.0(2)	88.5(1)	88.6(1)	88.6(1)	89.9(1)
O(1)–M(1)–O(15)	179.4(1)	179.5(3)	179.88(9)	179.6(1)	179.6(1)	179.4(1)
O(5)–M(1)–O(6)	178.7(1)	178.9(3)	178.7(1)	178.81(9)	178.8(2)	178.6(1)
O(5)–M(1)–O(10)	89.3(1)	89.3(2)	89.2(1)	89.4(1)	89.8(2)	89.8(1)
O(5)–M(1)–O(11)	90.5(1)	90.4(2)	90.5(1)	90.3(1)	89.5(2)	89.4(1)
O(5)–M(1)–O(15)	88.4(1)	88.6(2)	88.7(1)	89.1(1)	89.1(2)	89.3(1)
O(6)–M(1)–O(10)	90.8(1)	91.0(2)	90.6(1)	90.5(1)	90.6(2)	90.4(1)
O(6)–M(1)–O(11)	89.5(1)	89.4(2)	89.6(1)	89.8(1)	90.2(1)	90.5(1)
O(6)–M(1)–O(15)	90.4(1)	90.3(2)	90.0(1)	89.7(1)	89.8(1)	89.3(1)
O(10)–M(1)–O(11)	177.9(2)	177.8(2)	177.9(1)	177.9(1)	177.3(2)	177.7(1)
O(10)–M(1)–O(15)	90.5(1)	90.7(2)	90.6(1)	90.7(1)	91.3(2)	91.2(1)
O(11)–M(1)–O(15)	91.6(2)	91.5(2)	91.3(1)	91.4(1)	91.3(2)	90.9(1)

[a] Sample **2** is isomorphous with sample **1**.

refinement. Structure **2** has a relatively high *R* value due to a poor crystal and thus data. That is why we analyzed two structures with similar WDS analysis. As can be seen from the data in Tables 3 and 4 the cell parameters, *etc.* were similar to those of Structure **1**. Refinement of positional and anisotropic thermal parameters led to convergence (see Table 3).

CCDC reference numbers 158418–158424.

Microprobe analyses

After X-ray data collection the single crystals were mounted on a piece of conductive carbon tape and coated with a layer of pure carbon, approximately 25 nm thick, by vacuum evaporation, in order to provide electrical conductivity. The crystals were then subjected to quantitative analysis with a Sun computer based Cameca SX50 electron microscope equipped with a PGT energy dispersive spectrometer (EDS). The operating conditions used were a 10 μm diameter beam at 15 kV accelerating voltage and 15 nA beam current measured in a column mounted faraday cup. The beam current and size were chosen to minimize damage to the specimen during data acquisition. The chemistry present was carefully analyzed by WDS techniques on the electron microscope.

The wavelength spectrometers were calibrated to the X-ray lines for the respective elements using standard microprobe techniques. The calibrations were acquired by a 5-point average of counting on X-ray peaks for the given element for 20 seconds then correcting for the background intensity. Compositions of the "unknowns" were determined by acquiring counts for 20 seconds on the X-ray peak of each element and 20 seconds for the background intensities as well. From these data the computer using the PAP method (data reduction program) then calculates the composition of each analyzed point on the unknown.

References

1 D. C. Bradley, *Chem. Rev.*, 1989, **89**, 1317.
2 G. S. Girolami and J. E. Gozum, *Mater. Res. Soc.*, *Symp. Proc.*, 1990, **168**, 319.
3 A. R. Barron and W. S. Rees, Jr., *Adv. Mater. Optic. Electron.*, 1993, **2**, 271.
4 K. Haga, F. Katahira and H. Watanabe, *Thin Solid Films*, 1999, **343–344**, 145.
5 L. M. Tonge, D. S. Richeson, T. J. Marks, J. Zhao, B. W. Wessels, H. O. Marcy and C. R. Kannewurf, *Adv. Chem. Ser.*, 1990, **226**, 351.
6 O. B. Ajayi, M. S. Akanni, J. N. Lambi, C. Jeynes and J. F. Watts, *Thin Solid Films*, 1990, **185**, 123.
7 G. G. Condorelli, G. Malandrino and I. Fragala, *Chem. Mater.*, 1994, **6**, 1861.
8 T. Maruyama and Y. Ikuta, *J. Mater. Sci.*, 1993, **28**, 5073.
9 T. Maruyama and S. Arai, *Appl. Phys. Lett.*, 1992, **60**, 322.
10 K. R. Dunbar and S. C. Haefner, *Inorg. Chem.*, 1992, **31**, 3676.
11 K. Yoon and G. Parkin, *Inorg. Chem.*, 1992, **114**, 31.
12 F. A. Cotton, L. R. Favello, C. A. Murillo and G. Valle, *Z. Anorg. Allg. Chem.*, 1986, **540/541**, 67.
13 F. A. Cotton, L. R. Favello, E. L. Ohlhausen, C. A. Murillo and J. Quesada, *Z. Anorg. Allg. Chem.*, 1991, **598/599**, 53.
14 M. A. Araya, F. A. Cotton, L. M. Daniels, L. R. Favello and C. A. Murillo, *Inorg. Chem.*, 1993, **32**, 4853.
15 F. A. Cotton, L. M. Daniels, L. R. Favello, C. A. Murillo and A. J. Schultz, *Inorg. Chem.*, 1994, **33**, 5396.
16 B. D. Fahlman, S. G. Bott and A. R. Barron, *J. Chem. Cryst.*, 2000, **30**, 65.
17 M. P. Trubelja, E. Ryba and K. D. Smith, *J. Mater. Sci.*, 1996, **31**, 1435.
18 P. K. Hon and C. E. Pfluger, *J. Coord. Chem.*, 1973, **3**, 67.
19 A. Rahman, S. N. Ahmed, M. A. Khair, E. Zangrando and L. Randaccio, *J. Bangladesh Acad. Sci.*, 1990, **14**, 161.
20 B. Morosin, *Acta Crystallogr.*, 1965, **19**, 131.
21 C. C. Landry, J. Lockwood and A. R. Barron, *Chem. Mater.*, 1995, **7**, 699.
22 J. Glusker, M. Lewis and M. Rossi, *Crystal Structure Analysis for Chemists and Biologists*, VCH, New York, 1994.
23 *Handbook of Chemistry and Physics*, CRC Press, Boca Raton, FL, 60th edn., 1980.
24 J. E. Aron, J. C. Wolley, A. Asbjornson, S. Chatraphorn, K. Ratanathammapan and K. Yoodee, *J. Appl. Phys.*, 1981, **52**, 6223.
25 M. R. Mason, J. M. Smith, S. G. Bott and A. R. Barron, *J. Am. Chem. Soc.*, 1993, **115**, 4971.
26 G. M. Sheldrick, *Acta Crystallogr., Sect. A*, 1990, **46**, 467.
27 G. M. Sheldrick, SHELXTL, Bruker AXS, Inc., Madison, WI, 1997.