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Chloro[*N*,*N*′-ethylenediimino-bis(acetylacetonato)]gallium(III)

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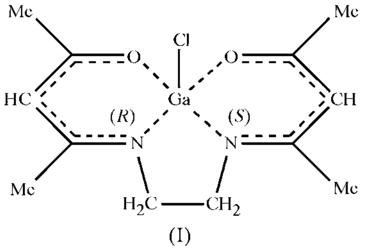
In the title compound, [Ga($C_{12}H_{18}N_2O_2$)Cl], the Ga atom is coordinated to a Cl atom and the two imine N and two enolate O atoms of the Schiff base ligand. The literature reveals few examples of a five-coordinate GaO_2N_2Cl environment, and only two where both the N and the O atoms are contained within the same ligand. This configuration has the effect of constraining the complex into a square-pyramidal geometry with less distortion than if formed by two or more ligands. The Ga—N and Ga—O distances are within the ranges expected for Ga–Schiff base derivatives. This compound is also the first group 13 complex containing the *N*,*N*′-ethylenebis(acetylacetoneimine) (acacen) ligand.

Comment

There has been recent interest in the design of methodology *en route* toward metal oxynitrides, possessing intermediate properties between oxide and nitride phases (Kim *et al.*, 2000; Pan *et al.*, 1985; Erlat *et al.*, 2004). Novel materials composed of group 13 oxynitrides have recently been used as supports for catalytic applications (Delsarte *et al.*, 2003; Centeno *et al.*, 2000) and high-temperature ceramics (Cao & Metselaar, 1991; Hwang & Chen, 1994; Ryabora & Savitskaya, 1968). The sputter deposition of aluminium oxynitride films on to polymer matrices has recently been found to impart superior water vapor permeation resistance (Delsarte *et al.*, 2003).



(I)

We are focused on the design of single-source precursors for oxynitride films and nanostructural materials. Suitable compounds must contain both *M*—O and *M*—N units; for certain applications, the backbone of the ligand should also contain small amounts of carbon. For oxide thin films, metal β-diketonate complexes have been widely used because of their low cost, stability, high volatility, low toxicity and lack of *M*—C bonds (Barron, 1996). Furthermore, the volatility of these complexes has been found to change dramatically upon substitution of fluorine for hydrogen groups, allowing for fine tuning of the deposition conditions (Fahlman & Barron, 2000).

Compounds that contain the Schiff base ligand *N*,*N*′-ethylenebis(acetylacetoneimine) (acacen) may represent a suitable class of materials for oxynitride-based materials, because of the relatively low carbon content and the presence of direct *M*—O and *M*—N bonds. This ligand system has been well studied, as numerous transition metal (Baker *et al.*, 1970; Larkworthy *et al.*, 1984; Gambarotta *et al.*, 1985) and rare earth complexes (Cai *et al.*, 2001; Junk & Smith, 2003) have been isolated. Metal–acacen complexes are comparable to those containing the salen [bis(salicylidene)ethylenediamine] family of ligands, which are widely employed for catalytic applications (Atwood & Harvey, 2001). We have now synthesized the title complex, (I), and it represents the first use of this ligand on a group 13 metal, and only the second on a main-group metal (Ewings *et al.*, 1976). The most common method used to synthesize metal–acacen complexes consists of exothermic reactions between the neutral acacenH_2 and a metal alkyl (Baker *et al.*, 1970; Larkworthy *et al.*, 1984; Gambarotta *et al.*, 1985; Cai *et al.*, 2001; Junk & Smith, 2003). However, this route was not successful with regard to the group 13 analogs, and we instead used the reaction of an Na_2(acacen) salt with the corresponding metal chloride.

A number of points regarding the structure and bonding in (I) (Fig. 1) are relevant. The compound contains a five-coordinate Ga atom in a distorted square-pyramidal geometry, with the ligand occupying the basal plane at a Ga–N_2O_2 plane distance of 0.47 Å. The Cl atom occupies the apical site at a distance of 2.2237 (4) Å. The average Ga—O and Ga—N bond distances are 1.91 and 2.00 Å, respectively, and are comparable to those of analogous salen derivatives (Atwood & Harvey). When comparing this structure with other complexes with GaN_2O_2Cl coordination environments, it is apparent that having a single N_2O_2 four-coordinate ligand

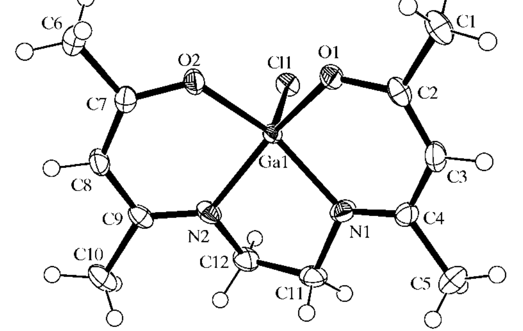


Figure 1
The molecular structure of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii. Atoms of the lower fraction of the disordered part of the molecule have been omitted for clarity.

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lessens the level of distortion from the ideal square-pyramidal geometry. Indeed, in systems where the ligands are allowed to rotate more freely, the geometry is much more distorted. Furthermore, when comparing this group 13 metal–acacen complex with one of the numerous five-coordinate transition metal complexes, the geometries are very similar (Clark *et al.*, 1969; Sato *et al.*, 1981). Thus far, our attempts to grow single crystals of the aluminium analogue have not been successful.

Experimental

For the preparation of the title compound, which was carried out under an inert atmosphere, Na_2(acacen) (2.149 g, 8.01 mmol), prepared from the reaction of *N*,*N*′-ethylenebis(acetylacetoneimine) and NaH, was added slowly *via* a solid addition funnel to a stirred solution of $GaCl_3$ (1.49 g, 8.00 mmol) in benzene. The reaction was then stirred overnight at room temperature. The yellow solution was filtered and the precipitant was washed with benzene to extract additional product. The solution was dried *in vacuo* and recrystallized *via* sublimation to yield yellow crystals suitable for X-ray crystallographic analysis.

Crystal data

$[Ga(C_{12}H_{18}N_2O_2)Cl]$
$M_r = 327.45$
Monoclinic, $P2_1/n$
$a = 7.2163$ (6) Å
$b = 24.102$ (2) Å
$c = 8.0669$ (7) Å
$\beta = 101.7760$ (10)°
$V = 1373.5$ (2) Å^3
$Z = 4$
$D_x = 1.584$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 2980 reflections
$\theta = 1.7$–28.3°
$\mu = 2.19$ mm^{-1}
$T = 163$ (2) K
Plate, light yellow
0.33 × 0.20 × 0.12 mm

Data collection

Bruker SMART CCD diffractometer
φ and ω scans
Absorption correction: empirical [using intensity measurements (*SADABS*; Bruker, 1998)]
$T_{\min} = 0.531$, $T_{\max} = 0.779$
14 190 measured reflections
3298 independent reflections
2992 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.024$
$\theta_{\max} = 28.3°$
$h = -9 \rightarrow 9$
$k = -31 \rightarrow 31$
$l = -10 \rightarrow 10$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.020$
$wR(F^2) = 0.051$
$S = 1.08$
3298 reflections
239 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0217P)^2 + 0.5951P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.32$ e Å^{-3}
$\Delta\rho_{\min} = -0.25$ e Å^{-3}

A measure of disorder was observed for atoms C11 and C12 and their adjacent positions, with occupancies of approximately 60:40. H atoms on disordered C atoms were placed in calculated positions and treated using a riding model (C—H = 0.97 Å). All other H atoms were freely refined [C—H = 0.88 (3)–1.05 (3) Å].

Data collection: *SMART* (Bruker, 1998); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 1998); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 1998); software used to prepare material for publication: *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: HJ1048). Services for accessing these data are described at the back of the journal.

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