

Discussion. Fig. 1 is a *PLUTO* projection (Motherwell & Clegg, 1978) of the dinuclear compound $[\text{Cu}_2(\text{tped})(\text{H}_2\text{O})_2(\text{NO}_3)_2](\text{NO}_3)_2 \cdot 2\text{CH}_3\text{OH}$. This compound has a centre of symmetry. In the asymmetric unit $[\text{Cu}(\text{tped})_{0.5}(\text{H}_2\text{O})(\text{NO}_3)](\text{NO}_3) \cdot \text{CH}_3\text{OH}$ the Cu ion is in a distorted, $\tau = 0.26$ (Addison, Rao, Reedijk, van Rijn & Verschoor, 1984), square pyramid of two pyrazole N atoms and an amine N atom of the ligand tped, an O atom of a water molecule and an O atom of one of the nitrate anions. The amine N atom occupies the apex of the square pyramid, and the Cu ion lies well above the N(12)—N(22)—O(91)—O(4) plane. Therefore, the coordination geometry around Cu(1) is distorted square pyramidal rather than distorted octahedral, although the Cu(1)—O(93) distance of 2.629 (3) Å could be regarded as semi-coordinating. The distances from the Cu ion to the pyrazole N atoms and to the amine N atom are 1.993 (4), 2.013 (3) and 2.303 (3) Å, respectively. Which are comparable to metal–nitrogen distances in coordination compounds of related ligands (Haanstra *et al.*, 1991; Hulsbergen *et al.*, 1984; Hendriks *et al.*, 1982; Birker, Hendriks, Reedijk & Verschoor, 1981). The distances of 1.947 (3) and 2.063 (3) Å of, respectively, the water O atom to Cu and the nitrate O atom to Cu are also comparable to such distances in related compounds (Driessen, de Graaff, Ochocki & Reedijk, 1988; Kleywegt, Wiesmeijer, van Driel, Driessen, Noordik & Reedijk, 1985). The coordination angles spanned by the pyrazole-N to amine-N bites of the ligand are 90.0 (1) and 95.5 (1)°; indeed, substantially larger than encountered with ligands with three-bond bites (Hulsbergen *et al.*, 1984; Hendriks *et al.*, 1982; Birker *et al.*, 1981).

The ligand tped accommodates two Cu ions at a distance of 6.563(1) Å, indicating that the CuN_3O_2 chromophores are well separated. The coordinated water molecule O(4) is hydrogen bonded to the

non-coordinated nitrate O(82) anion and to the methanol molecule O(5). The methanol molecule is hydrogen bonded to O(93) of the nitrate anion which is coordinated through O(91) to Cu(1). The water–methanol–nitrate hydrogen bonds and the ligand link the asymmetric units together in a zigzag chain, which lies in a plane perpendicular to the *b* axis.

The pyrazole rings are planar with distances to the least-squares planes of less than 0.02 Å and there is no stacking between the rings; the crystal packing is thus determined by van der Waals contacts and hydrogen bonding.

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Structure of Methylbis(salicylaloximato-*O*¹,*N*)gallium(III)

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Abstract. $[\text{Ga}(\text{C}_7\text{H}_6\text{NO}_2)_2(\text{CH}_3)]$, $M_r = 357.01$, monoclinic, $C2/c$, $a = 14.760$ (1), $b = 12.486$ (1), $c = 8.5623$ (7) Å, $\beta = 101.780$ (4)°, $V = 1544.8$ (2) Å³, Z

$= 4$, $D_x = 1.535$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.71073$ Å, $\mu = 17.91$ cm⁻¹, $F(000) = 728$, $T = 294$ K, $R = 0.027$, $wR = 0.034$, for 1190 reflections with $I \geq 3\sigma(I)$. The

Table 1. Final positional (fractional $\times 10^4$, Ga $\times 10^5$) and equivalent isotropic thermal parameters ($\text{\AA}^2 \times 10^3$) with e.s.d.'s in parentheses

$$U_{\text{eq}} = (1/3) \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

| | x | y | z | U_{eq} |
|------|----------|-----------|----------|-----------------|
| Ga | 0 | 29798 (3) | 25000 | 56 |
| O(1) | 1248 (1) | 3492 (2) | 3253 (2) | 76 |
| O(2) | -660 (2) | 3711 (2) | -861 (2) | 79 |
| N | 144 (1) | 3595 (2) | 324 (2) | 58 |
| C(1) | 1946 (2) | 3596 (2) | 2489 (3) | 59 |
| C(2) | 1796 (2) | 3764 (2) | 841 (3) | 57 |
| C(3) | 2558 (2) | 3922 (2) | 116 (4) | 72 |
| C(4) | 3444 (2) | 3909 (3) | 1001 (4) | 81 |
| C(5) | 3587 (2) | 3725 (3) | 2615 (4) | 80 |
| C(6) | 2855 (2) | 3572 (2) | 3356 (4) | 71 |
| C(7) | 883 (2) | 3816 (2) | -159 (3) | 62 |
| C(8) | 0 | 1421 (4) | 2500 | 84 |

Table 2. Bond lengths (\AA) and angles ($^\circ$) with e.s.d.'s in parentheses

| | | | |
|---------------|------------|----------------|-----------|
| Ga—O(1) | 1.932 (2) | C(1)—C(6) | 1.395 (3) |
| Ga—N | 2.067 (2) | C(2)—C(3) | 1.405 (4) |
| Ga—C(8) | 1.947 (5) | C(2)—C(7) | 1.444 (3) |
| O(1)—C(1) | 1.336 (3) | C(3)—C(4) | 1.371 (4) |
| O(2)—N | 1.402 (2) | C(4)—C(5) | 1.375 (5) |
| N—C(7) | 1.274 (3) | C(5)—C(6) | 1.373 (4) |
| C(1)—C(2) | 1.400 (3) | | |
| O(1)—Ga—N | 84.94 (7) | O(2)—N—C(7) | 113.4 (2) |
| O(1)—Ga—C(8) | 109.33 (7) | O(1)—C(1)—C(2) | 122.0 (2) |
| O(1)—Ga—O(1') | 141.3 (1) | O(1)—C(1)—C(6) | 119.5 (2) |
| O(1)—Ga—N' | 80.91 (8) | C(2)—C(1)—C(6) | 118.5 (2) |
| N—Ga—C(8) | 111.83 (6) | C(1)—C(2)—C(3) | 119.4 (2) |
| N—Ga—O(1') | 80.91 (8) | C(1)—C(2)—C(7) | 122.8 (2) |
| N—Ga—N' | 136.3 (1) | C(3)—C(2)—C(7) | 117.8 (2) |
| C(8)—Ga—O(1') | 109.33 (7) | C(2)—C(3)—C(4) | 120.8 (3) |
| C(8)—Ga—N' | 111.83 (6) | C(3)—C(4)—C(5) | 119.5 (3) |
| Ga—O(1)—C(1) | 130.3 (1) | C(4)—C(5)—C(6) | 120.9 (3) |
| Ga—N—O(2) | 117.6 (2) | C(1)—C(6)—C(5) | 120.9 (3) |
| Ga—N—C(7) | 128.7 (2) | N—C(7)—C(2) | 123.8 (2) |

Symmetry code: (') $-x, y, \frac{1}{2} - z$.

methylbis[salicylaldoximato(1-)-*O*¹,*N*]gallium(III) molecule has exact *C*₂ symmetry. The coordination about the Ga atom is distorted square pyramidal with the Ga atom displaced 0.7068 (4) \AA from the mean plane of the basal donor set toward the apical methyl C atom. Bond lengths involving Ga are Ga—O = 1.932 (2), Ga—N = 2.067 (2) and Ga—C = 1.947 (5) \AA . The *trans* bond angles about Ga involving the basal atoms are O—Ga—O = 141.3 (1) and N—Ga—N = 136.3 (1)°.

Introduction. We report here the structure of the mononuclear five-coordinate Ga complex methylbis(salicylaldoximato-*O*¹,*N*)gallium(III). Relatively few five-coordinate Ga complexes have been structurally characterized. Most of the reported examples have polynuclear structures, the majority of these being dimeric in the solid state (Rettig, Storr & Trotter, 1974, 1975*a*, 1976, 1984; Rettig, Storr, Trotter & Urich, 1984; Banta, Rettig, Storr & Trotter, 1985; Onyiriuka, Rettig, Storr & Trotter, 1987). Two polymeric examples have been reported (Breakell, Rettig, Storr & Trotter, 1977; Boardman, Jeffs, Small & Worrall, 1984) in addition to a hexanuclear complex

containing two pentacoordinate and four tetracoordinate Ga atoms (Rettig, Storr & Trotter, 1975*b*). The first structurally characterized five-coordinate Ga complex was the mononuclear compound bis(2-methyl-8-quinolinato)chlorogallium(III) (Shiro & Fernando, 1971; Dymock & Palenik, 1973). Five more mononuclear examples have subsequently been reported (McPhail, Miller, Pitt, Gupta & Srivastava, 1976; Chong, Rettig, Storr & Trotter, 1981; Wynne, 1984; Coutsolelos, Guillard, Boukhris & Lecomte, 1986; Boukhris, Lecomte, Coutsolelos & Guillard, 1986), the three most recent being porphyrin derivatives.

Experimental. Methylbis(salicylaldoximato-*O*¹,*N*)gallium(III) was prepared by the reaction of salicylaldoxime with trimethylgallium in tetrahydrofuran. A pale-yellow plate, 0.11 \times 0.40 \times 0.42 mm, was used for data collection on an Enraf-Nonius CAD-4F diffractometer. Lattice parameters were determined from 25 reflections with $\theta = 18$ –22°. Intensities were collected for $\theta \leq 30^\circ$, *hkl*: 0 to 20, 0 to 17, -12 to 12, using ω -2 θ scan, ω -scan width $(0.90 + 0.35 \tan \theta)^\circ$ at 1.2–10.0° min⁻¹; scan extended by 25% on each side for background measurement. Three standard reflections showed only small random fluctuations in intensity. Lp and absorption corrections (analytical, transmission factors 0.459–0.832) were applied. 2248 independent reflections were measured, 1190 with $I \geq 3\sigma(I)$; $\sigma^2(F_o^2) = [S^2(C + 4B) + (0.04F_o^2)^2]/Lp^2$, S = scan speed, C = scan count, B = background count. The structure was solved by Patterson and Fourier syntheses, and refined by full-matrix least squares on $w(\Delta F)^2$, $w = 4F_o^2/\sigma(F_o^2)$, with H atoms refined with isotropic thermal parameters (the methyl H atoms were 1:1 disordered about the twofold axis).

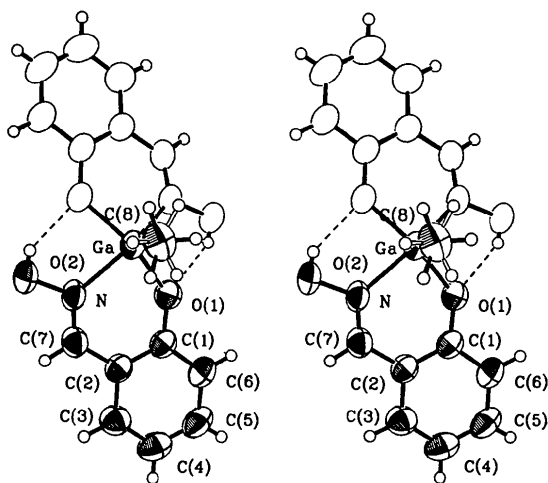


Fig. 1. Stereoview of methylbis(salicylaldoximato-*O*¹,*N*)gallium(III); 50% probability thermal ellipsoids are shown for the non-H atoms. Dashed lines represent hydrogen bonds.

Table 3. Structural parameters for five-coordinate Ga complexes

| Complex | Type* | Geometry† | Ga bond lengths (Å) | | | | | | Angles (°) axial—Ga—axial trans basal angles |
|---------|----------|-----------|---------------------|----------------|-----------------|----------------|----------------|----------------------|--|
| | | | Axial | | | Equatorial | | | |
| | | | Apical | Basal | | Equatorial | | | |
| (a) | <i>m</i> | TBP | Ga—N 2.119 (8) | Ga—N 2.110 (9) | Ga—Cl 2.195 (5) | Ga—O 1.855 (8) | Ga—O 1.879 (9) | 169 (1) | |
| (b) | <i>b</i> | TBP | N 2.192 (5) | O 2.018 (2) | O 1.960 (8) | O 1.847 (2) | H 1.41 (4) | 151.2 (4) | |
| (c) | <i>b</i> | TBP | N 2.279 (3) | O 2.053 (3) | O 1.911 (3) | H 1.50 (7) | H 1.73 (5) | 152.4 (1) | |
| (d) | <i>b</i> | TBP | N 2.471 (4) | O 2.078 (3) | O 1.913 (3) | C 1.936 (6) | C 1.948 (7) | 150.0 (1) | |
| (e) | <i>p</i> | TBP | N 2.778 (3) | O 1.987 (3) | N 1.996 (3) | N 1.945 (3) | H 1.49 (5) | 175.9 (1) | |
| (f) | <i>m</i> | TBP | Cl 2.440 (3) | N 2.433 (6) | N 2.119 (6) | C 1.956 (9) | C 1.95 (1) | 161.0 (2) | |
| (g) | <i>b</i> | TBP | O 2.469 (3) | O 2.127 (3) | O 1.933 (3) | C 1.944 (5) | C 1.946 (5) | 164.4 (1) | |
| (h) | <i>p</i> | TBP | O 2.695 (3) | O 2.036 (3) | N 2.027 (3) | C 1.936 (5) | C 1.952 (5) | 157.7 (1) | |
| (i) | <i>m</i> | SP/TBP | Cl 2.223 (2) | N 2.014 (6) | N 2.030 (5) | O 1.863 (4) | O 1.879 (4) | 159.4 (2), 145.3 (2) | |
| (j) | <i>b</i> | TBP | O 2.545 (2) | O 2.020 (2) | O 1.963 (2) | C 1.943 (4) | C 1.946 (4) | 149.99 (5) | |
| (k) | <i>p</i> | TBP | O 2.210 (4) | O 2.210 (4) | Cl 2.152 (3) | Cl 2.159 (2) | Cl 2.159 (2) | Not available | |
| (l) | <i>m</i> | SP | Cl 2.217 (1) | N 1.979 (4) | N 1.981 (4) | N 1.983 (4) | N 1.988 (4) | 154.5 (2), 154.3 (2) | |
| (m) | <i>b</i> | TBP | N 2.271 (3) | O 2.073 (3) | O 1.925 (3) | C 1.967 (4) | C 1.967 (4) | 148.8 (1) | |
| (n) | <i>b</i> | TBP | O 2.395 (3) | O 2.103 (3) | O 1.950 (3) | C 1.953 (5) | C 1.947 (5) | 150.2 (1) | |
| (o) | <i>m</i> | SP | O 1.908 (6) | N 2.015 (5) | N 2.021 (4) | N 2.017 (4) | N 2.000 (4) | 162.7, 160.6 | |
| (p) | <i>m</i> | SP | N 1.955 (2) | N 2.029 (1) | N 2.031 (1) | N 2.037 (1) | N 2.041 (1) | 159.0 (1), 160.0 (1) | |
| (q) | <i>b</i> | TBP | N 2.211 (3) | O 2.297 (3) | O 1.937 (3) | C 1.948 (6) | C 1.945 (5) | 149.7 (1) | |

(a) Bis(2-methyl-8-quinolinato)chlorogallium(III) (Shiro & Fernando, 1971; Dymock & Palenik, 1973).

(b) *N*-Methyldiethanolaminogallane dimer (Rettig, Storr & Trotter, 1974).

(c) Ethanolaminodimethylgallium dimer (Rettig, Storr & Trotter, 1975a).

(d) *N,N*-Dimethylethanolaminodimethylgallium dimer (Rettig, Storr & Trotter, 1975a).

(e) (GaH)₆(GaH₂)₂(μ-O)₂(μ₃-NCH₂CH₂NMe₂)₄(μ-NHCH₂CH₂NMe₂)₂ (Rettig, Storr & Trotter, 1975b).

(f) Chloro(dimethyl)(1,10-phenanthroline)gallium(III) (McPhail, Miller, Pitt, Gupta & Srivastava, 1976).

(g) (Salicylaldehydato)dimethylgallium dimer (Rettig, Storr & Trotter, 1976).

(h) *L*-Prolinatodimethylgallium polymer (Breakell, Rettig, Storr & Trotter, 1977).

(i) *N,N'*-Ethylenebis(salicylideneiminato)chlorogallium(III) (Chong, Rettig, Storr & Trotter, 1981).

(j) Bis(tropolonato)dimethylgallium (Rettig, Storr & Trotter, 1984).

(k) (μ-1,4-Dioxane-*O,O'*)trichlorogallium (Boardman, Jeffs, Small & Worrall, 1984).

(l) Chloro(phthalocyaninato)gallium(III) (Wynne, 1984).

(m) Bis[(μ-pyridine-2-methanolato)-dimethylgallium] (Rettig, Storr, Trotter & Uhrich, 1984).

(n) Bis[(μ-trimethylcitrate-*O,O'*)-dimethylgallium(III)] (Banta, Rettig, Storr & Trotter, 1985).

(o) (Methylsulfonato-*O*)(2,3,7,8,12,13,17,18-octaethylporphyrinato)gallium(III) (Coutsoulos, Guillard, Boukhris & Lecomte, 1986).

(p) Azido(octaethylporphyrinato)gallium(III) (Boukhris, Lecomte, Coutsoulos & Guillard, 1986).

(q) Bis[(μ-8-quinolinolato-*N,O,O'*)-dimethylgallium] (Onyiriuka, Rettig, Storr & Trotter, 1987).

* *b* = binuclear, *m* = mononuclear, *p* = polynuclear.

† TBP = trigonal bipyramidal, SP = square pyramidal.

Scattering factors were obtained from *International Tables for X-ray Crystallography* (1974, Vol. IV, pp. 99–102, 149). Computations were performed using locally written programs and locally modified versions of *ORFLS* (Busing, Martin & Levy, 1962), *ORFFE* (Busing, Martin & Levy, 1964) and *ORTEP* (Johnson, 1976). Final $R = 0.027$, $wR = 0.034$ for 1190 reflections, $S = 1.436$, 137 parameters, $R = 0.083$ for all 2248 reflections, $\Delta/\sigma_{\max} = 0.31$, final difference density -0.34 to 0.23 e Å⁻³.

Discussion. Final positional and equivalent isotropic thermal parameters are given in Table 1, and geometrical data appear in Table 2. A stereoview of the methylbis(salicylaloximate-*O*¹,*N*)gallium(III) molecule is shown in Fig. 1.* Structural parameters for all of the previously reported five-coordinate Ga

structures are compiled in Table 3. The coordination about the Ga atom is distorted square pyramidal with the Ga atom displaced 0.7068 (4) Å from the mean plane of the N₂O₂ basal donor set toward the apical methyl C atom. The Ga—O and Ga—N distances in methylbis(salicylaloximate-*O*¹,*N*)gallium(III) are within the ranges observed in other five-coordinate Ga compounds for chemically similar bonds. The apical Ga—C bond [1.947 (5) Å] is the first such bond to be reported and is similar in length to equatorial Ga—C distances in trigonal bipyramidal complexes (see Table 3). The two salicylaloximate ligands are linked by a pair of relatively strong O—H⋯O hydrogen bonds between the NOH groups and the Ga-coordinated phenolic O atoms [O(2)—H⋯O(1), O—H = 0.70 (3), H⋯O = 1.96 (3), O⋯O = 2.571 (3) Å, O—H⋯O = 146 (4)°]. The presence of these intramolecular hydrogen bonds, geometrically optimized when the two ligands are coplanar, is believed to be at least partially responsible for the square pyramidal coordination geometry adopted by this complex. The shortest intermolecular contact between non-H atoms is O(2)⋯C(7) = 3.245 (4) Å.

* Lists of H-atom parameters, anisotropic thermal parameters, bond lengths and angles involving H atoms, torsion angles, and structure factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55104 (16 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: HH0599]

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Structures of Aqua and Pyridine Adducts of Dimeric Copper(II) 2-Chlorobenzoate

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Abstract. Tetrakis(μ -2-chlorobenzoato-*O,O'*)-bis[aquacopper(II)], [Cu₂(C₇H₄ClO₂)₄(H₂O)₂], (I), $M_r = 785.4$, monoclinic, $P2_1/n$, $a = 7.214$ (2), $b = 19.554$ (4), $c = 10.877$ (4) Å, $\beta = 103.82$ (3)°, $V = 1489.9$ (7) Å³, $Z = 2$, $D_m = 1.75$ (2), $D_x = 1.75$ Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.71073$ Å, $\mu = 1.848$ mm⁻¹, $F(000) = 788$, $T = 298$ (2) K, $R = 0.032$ for 2536 observed reflections. Tetrakis(μ -2-chlorobenzoato-*O,O'*)-bis[pyridinecopper(II)] di(tetra-chloromethane), [Cu₂(C₇H₄ClO₂)₄(C₅H₅N)₂].2CCl₄, (II), $M_r = 1215.2$, monoclinic, $P2_1/a$, $a = 23.365$ (3), $b = 10.688$ (1), $c = 20.542$ (2) Å, $\beta = 100.03$ (1)°, $V = 5051.5$ (9) Å³, $Z = 4$, $D_x = 1.60$ Mg m⁻³, $\lambda(\text{Mo } K\alpha)$

$= 0.71073$ Å, $\mu = 1.533$ mm⁻¹, $F(000) = 2424$, $T = 299$ (2) K, $R = 0.074$ for 5124 reflections. The $-2J$ value of (I) observed by magnetic susceptibility measurement is abnormally small (262 cm⁻¹) among the copper benzoate complexes. This may be mainly a result of the bent structure of the Cu—O—C—O—Cu bridges.

Introduction. The exchange interaction in dimeric copper(II) carboxylates, [Cu(RCOO)₂L]₂, is anti-ferromagnetic. Quite recently, correlations between the $-2J$ value (the energy separation between the singlet and triplet states) and the molecular structure have been extensively studied, yielding a number of conclusions. The important factors which determine

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