Side-chain features also appear. It is striking how lysozyme shows a number of sharp-structured ROA features associated with tryptophan bands at ~1582, 1552, 1340, and 757 cm^{-1} (however, the positive ROA band at ~1340 cm^{-1} in lysozyme coincides in frequency with the strong positive ROA band in bovine serum albumin, which contains only one tryptophan residue, so it might not necessarily originate exclusively in tryptophan vibrations). There is also large negative ROA intensity associated with the side-chain CH_2 deformation band at ~1450 cm^{-1} in lysozyme and bovine serum albumin, but little in ribonuclease A.

Unfortunately we have not obtained ROA data on the important disulfide link in any of the proteins studied so far. The ROA is generally weak in the C-S stretch region[13] ~600-750 cm^{-1}, and measurements in the S-S stretch region[13] ~500-550 cm^{-1} are unreliable due to stray light. However, any ROA in these vibrations is likely to have a large isotropic component: isotropic ROA vanishes in backscattering, so measurements in forward scattering[17] might be necessary to detect disulfide ROA signals.

We have shown that protein ROA spectra can now be measured routinely and that they appear to contain new information about secondary backbone and side-group conformation. However, caution must be exercised in interpreting the observed features at this early stage, and we defer a detailed analysis until the ROA spectra of appropriate model peptides together with many more proteins have been acquired. Even at the rather coarse resolution used here to increase the intensity and hence reduce the acquisition time, much reproducible fine structure can be discerned (such as the steps on either side of the sharp negative ROA band at ~1240 cm^{-1} in lysozyme) which could contain subtle new information about conformations of the various structural elements. Higher resolution requires even better sensitivity, which would follow both from further instrument development and from ultrapurification of samples to reduce the background.

Acknowledgment. We thank the Science and Engineering Research Council and the Wolfson Foundation for research grants, the Deutsche Forschungsgemeinschaft for a postdoctoral scholarship (III 02-He 1588/1-1) for L.H., and Drs. A. Cooper and H. Sugeta for discussion.

---

(16) Chen, M. C.; Lord, R. C. *J. Am. Chem. Soc.* **1976**, *98*, 990-992.

(17) Barron, L. D.; Hecht, L.; Gargaro, A.; Hug, W. *J. Raman Spectrosc.* **1990**, *21*, 375-379.

Synthesis and Characterization of the First Main Group Oxo-Centered Trinuclear Carboxylate

Maria T. Andras,[†,‡] Stan A. Duraj,[*,§] Aloysius F. Hepp,[*,‡]
Phillip E. Fanwick,[∥] and Matthew M. Bodnar[§]

National Aeronautics and Space Administration
Lewis Research Center
Photovoltaic Branch, MS 302-1
Cleveland, Ohio 44135
Department of Chemistry
Cleveland State University
Cleveland, Ohio 44115
Department of Chemistry
Purdue University
West Lafayette, Indiana 47907

Received October 7, 1991

We report the synthesis and structural characterization of the first main group oxo-centered, trinuclear carboxylato-bridged species, namely, $[Ga_3(\mu_3\text{-}O)(\mu\text{-}O_2CC_6H_5)_6(4\text{-Mepy})_3]GaCl_4\cdot4\text{-Mepy}$ (**1**); 4-Mepy is 4-methylpyridine. Compound **1** is a main group example of a well-established class of complexes, referred to as "basic carboxylates" of the general formula $[M_3(\mu_3\text{-}O)(\mu\text{-}O_2CR)_6L_3]^+$, previously observed only for transition metals.[1,2]

Compound **1** was prepared in the following manner. Under argon, a solution of Ga_2Cl_4 (1.25 g, 4.44 mmol) and $C_6H_5CO_2Na$ (1.28 g, 8.88 mmol) in 35 mL of 4-methylpyridine was stirred for 3 days at 25 °C. The mixture was filtered; the resulting light gray residue was washed with hexanes and recrystallized from 4-methylpyridine/hexanes to produce white microcrystalline **1** in 80% yield.[3] Colorless, prismatic crystallographic-quality crystals were obtained by diffusion of hexanes into a 4-methylpyridine solution of $[Ga_3(\mu_3\text{-}O)(\mu\text{-}O_2CC_6H_5)_6(4\text{-Mepy})_3]GaCl_4\cdot4\text{-Mepy}$ over a period of 1 week.[4]

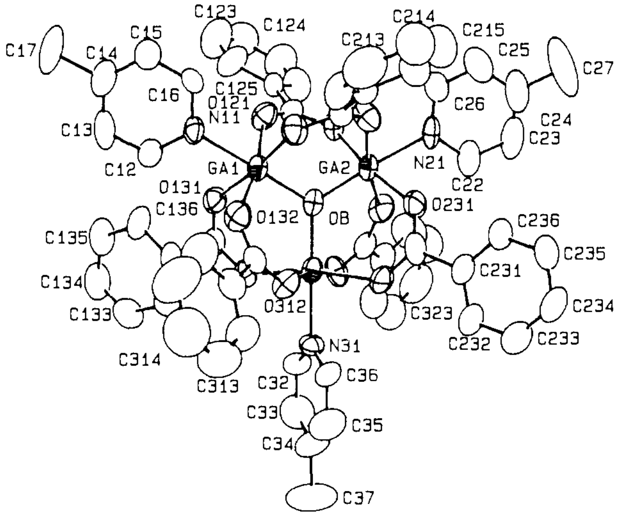


Figure 1. ORTEP drawing of the complex cation $[Ga_3(\mu_3\text{-}O)(\mu\text{-}O_2CC_6H_5)_6(4\text{-Mepy})_3]^+$, showing 50% thermal ellipsoids and the atomic-labeling scheme. Pertinent average bond distances (Å) and angles (deg) are as follows: Ga-O(B), 1.874 (8); Ga-O(benzoates), 1.985 (6); Ga-N, 2.08 (0); Ga···Ga, 3.246 (9); C-C, 1.37 (2) Å; C-O, 1.25 (2); Ga-Ga-Ga, 60.0 (3); Ga-Ga-O(B), 30.0 (3); Ga-O(B)-Ga, 120.0 (9); O-C-O, 126 (1); O(B)-Ga-N, 177.6 (9); O-C-C, 117 (2).

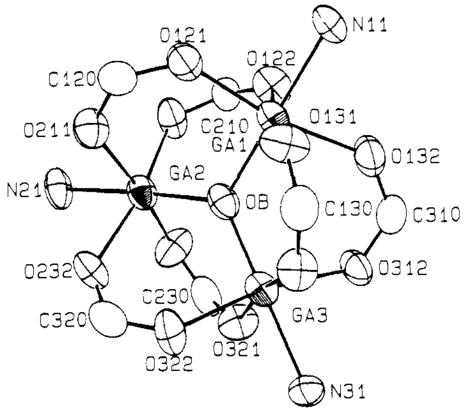


Figure 2. $Ga_3(\mu_3\text{-}O)(\mu\text{-}O_2C)_6N_3$ core of **1** showing the coordination sphere around the gallium atoms.

[†] This work was done while the author held a National Research Council-NASA Research Associateship.

[‡] NASA Lewis Research Center.

[§] Cleveland State University.

[∥] Purdue University.

(1) (a) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 5th ed.; Wiley: New York, 1988; pp 466-467. (b) Cannon, R. D.; White, R. P. *Prog. Inorg. Chem.* **1988**, *36*, 195-298. (c) Mehrotra, R. C.; Bohra, R. *Metal Carboxylates*; Academic Press: London, 1983.

(2) (a) Cotton, F. A.; Shang, M.; Sun, Z. S. *J. Am. Chem. Soc.* **1991**, *113*, 6917-6922. (b) Poganiuch, P.; Liu, S.; Papaefthymiou, G. C.; Lippard, S. J. *J. Am. Chem. Soc.* **1991**, *113*, 4645-4651. (c) Jang, H. G.; Geib, S. J.; Kaneko, Y.; Nakano, M.; Sorai, M.; Rheingold, A. L.; Montez, B.; Hendrickson, D. N. *J. Am. Chem. Soc.* **1989**, *111*, 173-180.

(3) Analytical results calculated (found) for $C_{60}H_{51}Cl_4Ga_4N_3O_{13}$: C, 49.95 (49.58); H, 3.56 (3.78); Cl, 9.83 (9.6).

(4) A single crystal (0.5 × 0.4 × 0.38 mm) of **1** was sealed in a glass capillary for data collection. Diffraction data were collected at 20 °C on an Enraf-Nonius CAD-4 diffractometer with graphite monochromatized Mo Kα radiation (λ = 0.71073 Å). A total of 5137 independent reflections with 2θ = 4-45° were collected. Crystal data: monoclinic, space group $P2_1$; a = 14.398 (2) Å, b = 17.638 (3) Å, c = 16.215 (2) Å, β = 113.15 (1)°; V = 3786 (2) Å^3; Z = 2; D_c = 1.347 g/cm^3; μ(Mo Kα = 16.01 cm^{-1}); R = 0.057 (R_w = 0.067) for 3776 reflections with $I > 3\sigma(I_o)$; GOF = 1.15.

0002-7863/92/1514-786$03.00/0

The solid-state molecular structure of the complex cation is shown in Figure 1. The central Ga_3O moiety consists of a planar, oxo-centered triangular arrangement of gallium(III) atoms; see Figure 2. The average Ga–Ga–Ga, Ga–Ga–O(B), and Ga–O(B)–Ga angles (see Figure 1) are within experimental error of the angles of an equilateral triangle. The μ_3-O atom is equidistant from the three gallium atoms; the average Ga–O(B) distance is 1.874 (3) Å.[5] Each edge of the Ga_3O core is bridged by two $C_6H_5CO_2^-$ ligands; the three axial positions are occupied by 4-methylpyridine molecules. Thus, each gallium(III) center possesses a slightly distorted octahedral coordination sphere.

The peripheral Ga–O distances range from 1.959 (5) to 2.006 (9) Å, with an average distance of 1.985 (6) Å. The observed distances are comparable to the average Ga–O distances found in other octahedrally-coordinated gallium(III) compounds.[6] The six bridging benzoato groups are equivalent as demonstrated by ^1H and ^{13}C NMR spectroscopy.[7] Within the benzoate groups, the average bond distances and angles are in accord with values reported for related complexes.[8]

As evidenced by Figure 1, there is a distinct difference in the orientation of the three axial 4-methylpyridine ligands around the Ga_3O core. Two of the 4-methylpyridine planes are approximately parallel to the Ga_3O plane; the dihedral angle is 10°. The plane of the third 4-methylpyridine is perpendicular to the plane; the dihedral angle is 90.1°.

Variable-temperature ^1H NMR studies of **1** indicate a rapid interconversion between the two orientations of the axial 4-methylpyridine ligands. At 34 °C, the ^1H NMR spectrum of **1** in solution is consistent with the solid-state structure shown in Figure 1.[7] Two sets of signals, in a 1:2 ratio, are observed for each of the three types of protons in the 4-methylpyridine ligands.[9] Increasing the temperature to 50 °C results in coalescence for each 4-methylpyridine (methyl and α and β ring: 2.63, 9.06, and 7.54 ppm, respectively) proton signal. Finally, as the probe is returned to ambient conditions, the original ^1H NMR spectrum is obtained.

The infrared spectrum[10] of **1**, between 800 and 4000 cm^{-1}, is dominated by bands attributable to the organic constituents of the cation.[11] We tentatively assign the strong bands at 1602, 1556, and 1420 cm^{-1} to bridging benzoate groups.[8a] Several IR bands below 800 cm^{-1} may be assigned by analogy to other $[M_3(\mu_3\text{-}O)(\mu\text{-}O_2CR)_6L_3]^+$ complexes.[11] These include an asymmetric stretch at 655 cm^{-1} of the central M_3O unit and the ν_d mode at 500 and 479 cm^{-1} of the MO_4 units. The band at 550 cm^{-1} occurs in almost all trimeric carboxylates and is assigned to a carboxylate mode.[1b,11]

In conclusion, we have observed a new reactivity pattern for Ga_2Cl_4. This simple one-step reaction demonstrates the accessibility of main group carboxylates of the general formula, $[M_3(\mu_3\text{-}O)(\mu\text{-}O_2CR)_6L_3]^+$, and constitutes a starting point in the discovery of related complexes. Investigations into the syntheses, characterization, and applications of related main group carboxylates are currently underway.

Acknowledgment. M.T.A. (Postdoctoral Fellowship, National Research Council/NASA Lewis Research Center), S.A.D. (NASA grant NCC3-162), and A.F.H. (Director's Discretionary Fund) acknowledge support from NASA Lewis Research Center. We thank Dr. David G. Hehemann and Mr. Frederick K. Oplinger of Cleveland State University for the NMR studies of **1**.

Supplementary Material Available: Tables of positional parameters, thermal parameters, and bond distances and angles (21 pages); tables of observed and calculated structure factors (17 pages). Ordering information is given on any current masthead page. Similar information is also available from A.F.H. at NASA Lewis Research Center.

---

[5] Individual Ga–O(B) and Ga···Ga bond distances: Ga(1)–O(B) 1.890 (9), Ga(2)–O(B) 1.866 (9), Ga(3)–O(B) 1.867 (9), Ga(1)–Ga(2) 3.228 (2), Ga(2)–Ga(3) 3.259 (2), and Ga(3)–Ga(1) 3.251 (2) Å.

[6] (a) Hausen, H. D.; Sille, K.; Weidlein, J.; Schwarz, W. *J. Organomet. Chem.* **1978**, *160*, 411-419. (b) Bulc, N.; Golic, L.; Siftar, J. *Acta Crystallogr.* **1984**, *C40*, 1829-1831. (c) Riley, P. E.; Pecoraro, V. L.; Carrano, C. J.; Raymond, K. N. *Inorg. Chem.* **1983**, *22*, 3096-3103.

[7] NMR data in $CDCl_3$: ^1H δ (ppm) 2.35 (s, 3 H, Me′), 2.67 (s, 6 H, Me), 7.12 (d, 2 H, β'), 7.35 (t, 12 H, meta), 7.48 (t, 6 H, para), 7.61 (d, 4 H, β), 7.84 (d, 12 H, ortho), 8.47 (d, 2 H, α'), 9.09 (d, 4 H, α); ^{13}C δ (ppm) 21.1, 21.7, 124.8, 125.4, 128.4, 130, 132.9, 133, 148.1, 149, 153, 173.5. The unique 4-methylpyridine ligand is indicated by (′).

[8] (a) Gorun, S. M.; Papaefthymiou, G. C.; Frankel, R. B.; Lippard, S. J. *J. Am. Chem. Soc.* **1987**, *109*, 3337-3348. (b) Vincent, J. B.; Christmas, C.; Huffman, J. C.; Christou, G.; Chang, H.-R.; Hendrickson, D. N. *J. Chem. Soc., Chem. Commun.* **1987**, 236-237.

[9] The ^1H NMR spectrum of $[Co_3(\mu_3\text{-}O)(\mu\text{-}O_2CCH_3)_5(OH)(py)_3]PF_6$ shows similar behavior; see: Sumner, C. E., Jr.; Steinmetz, G. R. *J. Am. Chem. Soc.* **1985**, *107*, 6124-6126.

[10] Infrared data (KBr, cm^{-1}): 3067 (m), 1664 (s), 1625 (vs, br), 1602 (vs, br), 1575 (vs), 1556 (s), 1551 (s), 1546 (s), 1536 (m), 1509 (m), 1495 (s), 1420 (vs, br), 1340 (m), 1329 (m), 1315 (m), 1309 (m), 1233 (m), 1215 (m), 1178 (s), 1070 (s), 1026 (s), 724 (vs), 688 (s), 683 (vs), 655 (vs), 550 (m), 500 (s), 479 (vs).

[11] (a) Johnson, M. K.; Powell, D. B.; Cannon, R. D. *Spectrochim. Acta* **1981**, *37A*, 995-1006. (b) Monti, L.; Cannon, R. D. *Ibid.* **1985**, *41A*, 643-646. (c) Meesuk, L.; Jayasooriya, V. A.; Cannon, R. D. *J. Am. Chem. Soc.* **1987**, *109*, 2009-2016.

Observation of β-Kinetic and β-Equilibrium Isotope Effects in Organometallic Oxidative Addition Reactions

Michael J. Hostetler and Robert G. Bergman*

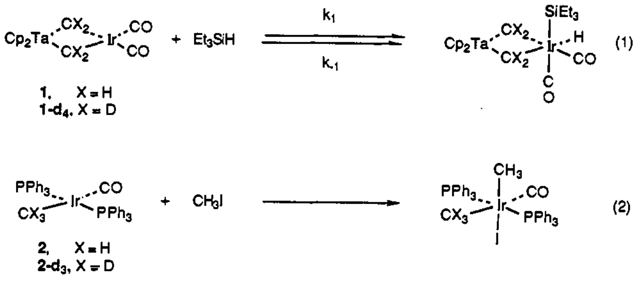
Department of Chemistry, University of California
Berkeley, California 94720

Received September 9, 1991

Secondary β-deuterium isotope effects have long been an important tool in the study of organic reaction mechanisms. Normal effects ($k_H/k_D > 1$) have been used to obtain evidence for hyperconjugation,[1a] and inverse effects ($k_H/k_D < 1$) have provided evidence for the steric[2] and inductive[3] influence of deuterium on the rates of organic transformations.[4] Both steric and inductive effects have been proposed to result from the shorter average length of a C–D bond (1.107 Å) relative to a C–H bond (1.112 Å).[5]

In contrast to their widespread use in organic chemistry, the employment of β-deuterium isotope effects to study transition-metal organometallic reactions has been essentially nonexistent.[6] We report an application of this technique to investigate both the rate and equilibrium of an organometallic transformation. The result of this work is an apparently general electron-donating effect of β-deuterium on oxidative addition reactions.

Scheme I



---

[1] Lowry, T. H.; Richardson, K. S. *Mechanism and Theory in Organic Chemistry*, 3rd ed.; Harper & Row: New York, 1987; (a) p 240, (b) p 257.

[2] Carter, R. E.; Melander, L. *Ad. Phys. Org. Chem.* **1973**, *10*, 1.

[3] Halevi, E. A. *Prog. Phys. Org. Chem.* **1963**, *1*, 109.

[4] Collins, C. J., Bowman, N. S., Eds. *Isotope Effects in Chemical Reactions*; Van Nostrand: New York, 1970.

[5] Obtained from electron diffraction studies on C_2H_6 and C_2D_6. Kuchitsu, K. *J. Chem. Phys.* **1968**, *49*, 4456.

[6] One report of such an effect for a transition-metal compound is for the reaction $H_2O + [Co(NX_3)_5Cl]^{2+} \rightarrow [Co(NX_3)_5(H_2O)]^{3+} + Cl^-$ (X = H, D), for which $k_H/k_D = 1.47$ in H_2O and $k_H/k_D = 1.19$ in D_2O. See: Pearson, R. G.; Stellwagen, N. C.; Basolo, F. *J. Am. Chem. Soc.* **1960**, *82*, 1077.

0002-7863/92/1514-787$03.00/0