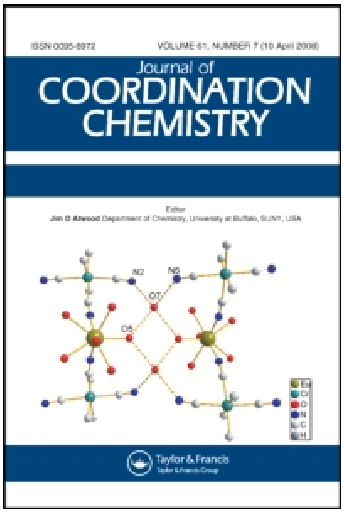
This article was downloaded by:
On: *23 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



## Journal of Coordination Chemistry

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

# Synthesis, Crystal Structure and Properties of a Pentanuclear Carboxylato-Bridged Complex Containing a $Cu_3Y_2$ Core

Cun-Gen Zhang[a]; Deyue Yan[a]; Yilin[a]; Fengyue Yang[a]
[a] College of Chemistry and Chemical Engineering, Shanghai Jiaotong University, Shanghai, P.R. China

**To cite this Article** Zhang, Cun-Gen , Yan, Deyue , Yilin and Yang, Fengyue(2000) 'Synthesis, Crystal Structure and Properties of a Pentanuclear Carboxylato-Bridged Complex Containing a $Cu_3Y_2$ Core', Journal of Coordination Chemistry, 51: 2, 261 — 269

**To link to this Article: DOI:** 10.1080/00958970008055132

**URL:** http://dx.doi.org/10.1080/00958970008055132

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

*J. Coord. Chem.*, 2000, Vol. 51, pp. 261–269
Reprints available directly from the publisher
Photocopying permitted by license only

# SYNTHESIS, CRYSTAL STRUCTURE AND PROPERTIES OF A PENTANUCLEAR CARBOXYLATO-BRIDGED COMPLEX CONTAINING A $Cu_3Y_2$ CORE

CUN-GEN ZHANG*, DEYUE YAN, YILIN MA
and FENGYUE YANG

*College of Chemistry and Chemical Engineering, Shanghai Jiaotong University,*
*Shanghai 200240, P.R. China*

*(Received 27 October 1999)*

Preparation and isolation of a pentanuclear mixed metal complex having the formula $[Cu_3Y_2(Cl{-}CH_2COO)_{12}(H_2O)_8]\cdot 2H_2O$ was accomplished by the reaction of a mixture of copper(II) nitrate and yttrium nitrate with sodium chloroacetate in aqueous solution. The structure of the complex was determined by X-ray crystallography. It consists of linear centrosymmetric pentanuclear molecules with a four-coordinate copper atom at the inversion site and the other two copper atoms having a 4 + 1 coordination geometry at both ends. Two yttrium atoms separate the three copper atoms. Each yttrium atom is bridged to the neighbouring terminal copper atom by four carboxylato ligands in a *syn–syn* fashion forming a dimer with the $Y \cdots Cu$ distance being 3.5311(8) Å. Each dimer is then linked to the central copper atom *via* a carboxylato bridging ligand in a *syn–anti* fashion. Two other carboxylato ligands coordinate to the central copper to complete its planar coordination. The apical site of each terminal copper atom is occupied by a water molecule. The eight-coordinate geometry of each yttrium atom is completed by three water molecules. Bridging and the monodentate carboxylato ligands were characterized by IR analysis. TG studies confirmed the numbers of coordinated and lattice water molecules.

*Keywords:* Copper; yttrium; chloroacetic acid; complex; X-ray structure

## INTRODUCTION

Heteronuclear complexes have received much attention not only in elucidating the magnetic coupling between metal ions[1–3] but also in model

---

* Corresponding author.

compounds for the active site of multi-metalloenzymes.[4,5] Among these, the nature of magnetic exchange interactions between *d*- and *f*-block metal ions *via* bridging ligands is most important because these complexes may be considered as possible precursors for high $T_c$ superconductors.[6] For the synthesis of heteronuclear complexes, two methods are generally employed. One uses a "ligand complex" which involves coordination ability to other metal ions. The other uses a polynucleating ligand exhibiting multi-coordination sites.[7] Nevertheless, the relatively easier synthetic method applying carboxylato ligands to bridge heteronuclear transition metal ions is seldom reported.[8–10] In this paper, we report the synthesis and properties of a new carboxylato-bridged pentanuclear $Cu_3Y_2$ complex $[Cu_3Y_2(Cl{-}CH_2COO)_{12}(H_2O)_8]\cdot 2H_2O$.

## EXPERIMENTAL

### Physical Measurements

C, H analyses were carried out with a Perkin-Elmer Model 240 instrument. Copper and lanthanide were determined by EDTA titration of an aqueous solution of copper(II) nitrate and lanthanide(III) nitrate, prepared in $HNO_3$ after the complexes were thermally decomposed. IR spectra were recorded on a Perkin-Elmer Paragon 1000 spectrophotometer with KBr discs. An X-ray crystal structure determination was carried out on a Siemens P4 diffractometer. Thermal studies were made on a Perkin-Elmer 7 Series System in $N_2$ atmosphere ($40\,cm^3\,min^{-1}$) and a heating rate of $20°C\,min^{-1}$.

### Preparation of the Complex $[Cu_3Y_2(Cl{-}CH_2COO)_{12}(H_2O)_8]\cdot 2H_2O$

To an aqueous solution containing equimolar copper(II) nitrate and yttrium nitrate was added five mol equivalents of sodium chloroacetate prepared by mixing sodium hydroxide and chloroacetic acid at room temperature. The resulting solution was filtered and allowed to stand at room temperature for a week. Well-shaped crystals were obtained by filtration. Overall yield: 75% based on copper. Found: C, 17.35; H, 2.71; Cu, 11.25; Y, 10.30%; Calcd. (based on $C_{24}H_{44}Cl_{12}Cu_3O_{34}Y_2$, $M_r = 1670.43$): C, 17.26; H, 2.66; Cu, 11.40%; Y, 10.65. IR spectra ($cm^{-1}$): 3620.4(s) ($\nu$OH); 3379.8(s), 2959.0(w) ($\delta$CH), 1676.3(s), 1614.5(s), 1401.3(s) (sym $\nu$CO); 1256.9(s), 1180.6(w), 969(w), 933.9(w), 796(m), 720(m), 685.6(m), 579(m).

### X-ray Crystallographic Study

A pale yellow crystal having dimensions 0.58 × 0.16 × 0.16 mm was mounted on a glass fibre. Unit cell parameters and the orientation matrix were determined by least-squares refinement using the setting angles of 38 centred reflections ($2.72° < \theta < 15.65°$) measured on a Siemens P4 diffractometer with graphite-monochromated MoK$\alpha$ radiation. Intensity data were collected at 296 K using a $\omega$–$2\theta$ scan technique up to a maximum $2\theta$ of 50°. Three standard reflections were monitored for crystal and instruments stabilities after every 97 data measurements. In all cases no significant variation was found. Some 5936 reflections were measured ($h \rightarrow 0$–$12$, $k \rightarrow -1$ to 21, $l \rightarrow -18$ to 17) which after data reduction ($R_{int} = 0.0205$) gave 4934 independent reflections. The intensity data were corrected for Lorentz and polarization effects and empirical absorption. Details on crystal data, intensity collection and refinement are listed in Table I. Some 3018 reflections with $I > 2\sigma(I)$ were used in the refinement of 429 parameters. The crystal structure was solved by direct methods and difference Fourier syntheses, and refined by full-matrix least-squares techniques using anisotropic temperature factors. All the hydrogen atoms were located using a riding mode. The final cycle of refinement converged at $R = 0.036$ and $R_w = 0.064$. All calculations were carried out using SHELXS-97,[11] SHELXL-97[12] and Siemens SHELXTL[13] programs. Complete tables of atomic coordinates and thermal parameters, exclude structure factors are available from the authors upon request.

## RESULTS AND DISCUSSION

### Structure Description

An ORTEP view of the complex with the atom numbering scheme is shown in Figure 1. Atomic coordinates and selected bond distances and angles are listed in Tables II and III, respectively. The complex contains three copper and two yttrium atoms in a linear arrangement, Cu···Y···Cu···Y···Cu. The central copper atom is four-coordinated by four carboxylato oxygen atoms, among which two are monodentate ligands and the other two are bridging ligands linking to the neighbouring yttrium atoms. Each terminal copper atom is linked to the adjacent yttrium atom *via* four carboxylato ligands with the Cu···Y distance being 3.5311(8) Å. All four chloroacetato ligands bridge the two heteronuclear atoms in a *syn–syn* fashion, different

TABLE I Crystal data and structure refinement details

| | |
|---|---|
| Compound | $[Cu_3Y_2(ClCH_2COO)_{12}(H_2O)_8]\cdot 2H_2O$ |
| Colour/shape | Green/prismatic |
| Empirical formula | $C_{24}H_{44}O_{34}Cl_{12}Cu_3Y_2$ |
| Formula weight | 1670.43 |
| Temperature | 296 K |
| Crystal system | Monoclinic |
| Space group | $P2_1/c$ |
| No. of reflections used for unit cell determination ($\theta$ range) | 38(2.72–15.65°) |
| $a$ Å | 10.471(2) |
| $b$ Å | 17.971(3) |
| $c$ Å | 15.233(2) |
| $\alpha$ (°) | 90 |
| $\beta$ (°) | 100.050(10) |
| $\gamma$ (°) | 90 |
| Volume (Å$^3$) | 2822.5(8) |
| $Z$ | 2 |
| $D_{calc}$ (g/cm$^3$) | 1.984 |
| $\mu$ (MoK$\alpha$) (cm$^{-1}$) | 38.06 |
| $F$(000) | 1674 |
| Radiation | MoK$\alpha$ ($\lambda = 0.71073$ Å) |
| Scan type | $\omega$ |
| $2\theta_{max}$ | 50° |
| No. of reflections measured | Total: 5936; unique: 4934 ($R_{int} = 0.0205$) |
| Correction | Semi-empirical from psi-scans |
| Structure solution | Direct methods (SHELXS-97) |
| Refinement | Full-matrix least-squares (SHELXL-97) |
| Refinement method | Full-matrix least-squares on $F^2$ |
| Treatment of H atoms | Riding mode and refined isotropically |
| No. observations $[I > 2\sigma(I)]$ | 3018 |
| No. variables | 429 |
| Goodness-of-fit on $F^2$ | 7.03 |
| Final $R$ indices $[I > 2\sigma(I)]$ | $R1 = 0.036$, $wR2 = 0.064$ |
| $R$ indices (all data) | $R1 = 0.075$, $wR2 = 0.070$ |
| Largest diff. Peak and hole | 0.677 and $-0.494\,e^-/Å^3$ |

from the *syn–anti* fashion found in the other two carboxylato ligands bridging the central copper and yttrium atoms. Two terminal copper atoms have a 4 + 1 coordination geometry in which a water molecule occupies the apical site. The yttrium atom has a eight-coordination double-cap triprismatic geometry, involving five carboxylato oxygen atoms and three water molecules. The coordination geometry is shown in Figure 2. The packing of the structure is mainly achieved by hydrogen bonding interactions.

## Infrared Spectra and Thermogravimetric Analysis

IR spectra of the complex clearly show the existence of the carboxylato ligands and water molecules. Carboxylate groups can coordinate to metal

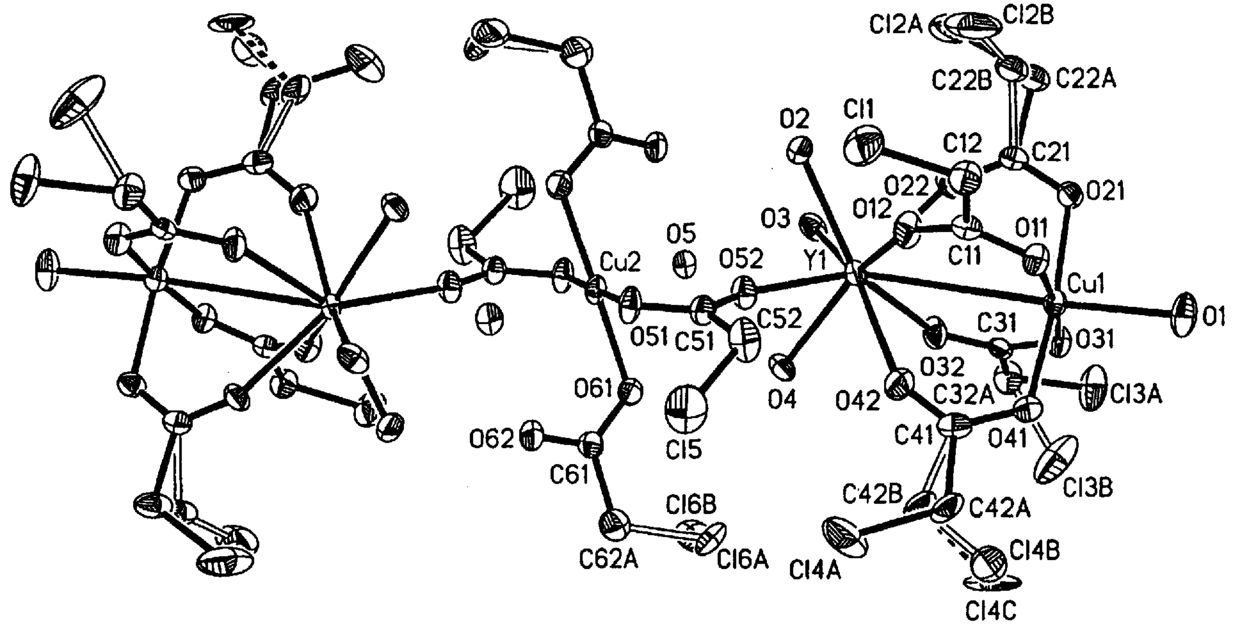


FIGURE 1 Molecular structure showing 50% probability displacement ellipsoids. H atoms bonded to C are omitted for clarity.

TABLE II Atomic parameters and equivalent isotropic thermal parameters

| *Atom* | $x/a$ | $y/b$ | $z/c$ | $U_{eq}$ (Å$^2$) |
|---|---|---|---|---|
| Y1 | 0.32167(4) | −0.13690(3) | 0.17732(3) | 0.02779(12) |
| Cu1 | 0.45252(5) | −0.27006(3) | 0.33867(3) | 0.03082(15) |
| Cu2 | 0.0000 | 0.0000 | 0.0000 | 0.0360(2) |
| O11 | 0.3443(3) | −0.22427(18) | 0.41822(19) | 0.0368(8) |
| O12 | 0.2732(3) | −0.13365(19) | 0.3225(2) | 0.0490(9) |
| C11 | 0.2846(4) | −0.1636(3) | 0.3962(3) | 0.0323(12) |
| C12 | 0.2308(5) | −0.1279(3) | 0.4711(3) | 0.0465(14) |
| Cl1 | 0.12468(16) | −0.05311(9) | 0.44023(10) | 0.0729(5) |
| O21 | 0.5859(3) | −0.19508(18) | 0.3805(2) | 0.0388(8) |
| O22 | 0.5147(3) | −0.11799(17) | 0.2697(2) | 0.0431(9) |
| C21 | 0.5863(4) | −0.1349(3) | 0.3399(3) | 0.0347(11) |
| C22A | 0. 6894(14) | −0.0813(5) | 0.3832(9) | 0.060(2) |
| Cl2A | 0.6758(3) | 0.00652(12) | 0.33139(15) | 0.1250(14) |
| C22B | 0.659(8) | −0.062(3) | 0.380(5) | 0.060(2) |
| Cl2B | 0.5499(11) | −0.0107(6) | 0.4320(10) | 0.146(8) |
| O31 | 0.5493(3) | −0.30616(18) | 0.2482(2) | 0.0432(9) |
| O32 | 0.4551(3) | −0.2300(2) | 0.1411(2) | 0.0484(9) |
| C31 | 0.5300(4) | −0.2807(2) | 0.1702(3) | 0.0339(12). |
| C32A | 0.6047(5) | −0.3132(3) | 0.1030(3) | 0.0516(15) |
| Cl3A | 0.7284(4) | −0.3745(2) | 0.1408(2) | 0.0760(17) |
| C32B | 0.6047(5) | −0.3132(3) | 0.1030(3) | 0.0516(15) |
| Cl3B | 0.5914(7) | −0.41013(19) | 0.0973(3) | 0.113(3) |
| O41 | 0.3052(3) | −0.33545(17) | 0.2931(2) | 0.0437(9) |
| O42 | 0.2153(3) | −0.24736(19) | 0.2003(2) | 0.0554(10) |
| C41 | 0.2165(4) | −0.3090(3) | 0.2362(3) | 0.0401(13) |
| C42A | 0.1029(14) | −0.3649(9) | 0.2228(11) | 0.056(3) |
| Cl4A | −0.0246(3) | −0.3329(2) | 0.1414(3) | 0.1129(17) |
| C42B | 0.0938(18) | −0.3499(9) | 0.1922(14) | 0.056(3) |
| Cl4B | 0.0588(6) | −0.4251(4) | 0.2571(4) | 0.068(3) |
| C42C | 0.0938(18) | −0.3499(9) | 0.1922(14) | 0.056(3) |
| Cl4C | 0.113(2) | −0.4467(6) | 0.205(3) | 0.102(11) |
| O51 | −0.0744(3) | −0.03761(18) | 0.1007(2) | 0.0424(9) |
| O52 | 0.1176(3) | −0.09039(18) | 0.1393(2) | 0.0401(8) |
| C51 | 0.0023(4) | −0.0825(3) | 0.1465(3) | 0.0363(12) |
| C52 | −0.0466(4) | −0.1295(3) | 0.2154(3) | 0.0609(17) |
| Cl5 | −0.21176(15) | −0.15005(10) | 0.18931(12) | 0.0893(6) |
| O61 | −0.0099(3) | −0.10078(17) | −0.0497(2) | 0.0427(9) |
| O62 | −0.2224(3) | −0.08075(19) | −0.0808(2) | 0.0508(10) |
| C61 | −0.1266(5) | −0.1204(2) | −0.0786(3) | 0.0411(13) |
| C62A | −0.1505(5) | −0.1986(3) | −0.1108(4) | 0.0675(17) |
| Cl6A | −0.0184(3) | −0.2555(2) | −0.1027(3) | 0.0969(17) |
| C62B | −0.1505(5) | −0.1986(3) | −0.1108(4) | 0.0675(17) |
| Cl6B | −0.070(2) | −0.2648(5) | −0.034(2) | 0.147(13) |
| O1 | 0.5462(3) | −0.3485(2) | 0.4404(2) | 0.0555(10) |
| O2 | 0.3263(4) | −0.0088(2) | 0.2184(2) | 0.0554(10) |
| O3 | 0.4407(3) | −0.0720(2) | 0.0805(2) | 0.0442(9) |
| O4 | 0.2389(3) | −0.1694(2) | 0.0266(2) | 0.0417(9) |
| O5 | 0.3385(4) | −0.02184(19) | −0.0912(2) | 0.0459(9) |

ions in a number of ways and IR spectroscopy is a useful tool in diagnosing the nature of carboxylate coordination. The separation between $\nu_{as}(COO^-)$ and $\nu_s(COO^-)$ when significantly less than the free carboxylate anion value is considered indicative of bidentate bridging or chelating carboxylate

TABLE III Selected bond distances (Å) and angles (°) for the complex

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| *Bond distances* | | | | | | | |
| Cu1 | O31 | 1.958(3) | Y1 | O22 | 2.278(3) | | |
| Cu1 | O21 | 1.965(3) | Y1 | O32 | 2.307(3) | | |
| Cu1 | O41 | 1.967(3) | Y1 | O42 | 2.332(4) | | |
| Cu1 | O11 | 1.977(3) | Y1 | O12 | 2.355(3) | | |
| Cu1 | O1 | 2.196(3) | Y1 | O4 | 2.381(3) | | |
| Cu2 | O51* | 1.958(3) | Y1 | O2 | 2.384(4) | | |
| Cu2 | O51 | 1.958(3) | Y1 | O3 | 2.394(3) | | |
| Cu2 | O61 | 1.959(3) | Y1 | Cu1 | 3.5311(8) | | |
| Cu2 | O61* | 1.959(3) | Y1 | O52 | 2.274(3) | | |
| *Bond angles* | | | | | | | |
| O52 | Y1 | O22 | 142.73(12) | O52 | Y1 | O32 | 141.93(12) |
| O22 | Y1 | O32 | 75.32(11) | O52 | Y1 | O42 | 84.20(12) |
| O22 | Y1 | O42 | 115.45(12) | O32 | Y1 | O42 | 75.16(13) |
| O52 | Y1 | O12 | 83.29(11) | O22 | Y1 | O12 | 74.30(12) |
| O32 | Y1 | O12 | 118.77(12) | O42 | Y1 | O12 | 72.14(12) |
| O52 | Y1 | O4 | 71.14(11) | O22 | Y1 | O4 | 140.07(11) |
| O32 | Y1 | O4 | 74.06(11) | O42 | Y1 | O4 | 80.38(13) |
| O12 | Y1 | O4 | 144.09(12) | O52 | Y1 | O2 | 71.76(13) |
| O22 | Y1 | O2 | 73.67(12) | O32 | Y1 | O2 | 141.01(14) |
| O42 | Y1 | O2 | 140.45(14) | O12 | Y1 | O2 | 74.20(13) |
| O4 | Y1 | O2 | 118.50(12) | O52 | Y1 | O3 | 103.37(11) |
| O22 | Y1 | O3 | 78.86(11) | O32 | Y1 | O3 | 78.67(13) |
| O42 | Y1 | O3 | 145.16(13) | O12 | Y1 | O3 | 141.95(12) |
| O4 | Y1 | O3 | 70.51(12) | O2 | Y1 | O3 | 72.67(14) |
| O31 | Cu1 | O21 | 91.68(13) | O31 | Cu1 | O41 | 91.39(14) |
| O21 | Cu1 | O41 | 173.40(14) | O31 | Cu1 | O11 | 172.58(13) |
| O21 | Cu1 | O11 | 88.10(13) | O41 | Cu1 | O11 | 88.10(13) |
| O31 | Cu1 | O1 | 93.55(13) | O21 | Cu1 | O1 | 90.36(14) |
| O41 | Cu1 | O1 | 95.28(15) | O11 | Cu1 | O1 | 93.87(13) |
| O51 | Cu2 | O51 | 180.0(3) | O51 | Cu2 | O61 | 88.98(13) |
| C11 | O11 | Cu1 | 120.2(3) | C11 | O12 | Y1 | 147.4(3) |
| C21 | O21 | Cu1 | 119.8(3) | C21 | O22 | Y1 | 147.1(3) |
| C31 | O31 | Cu1 | 121.9(3) | C31 | O32 | Y1 | 145.5(3) |
| C41 | O41 | Cu1 | 117.4(3) | C41 | O42 | Y1 | 149.6(3) |
| C51 | O51 | Cu2 | 110.6(3) | C51 | O52 | Y1 | 155.0(3) |
| C61 | O61 | Cu2 | 111.9(3) | | | | |

Symmetry code: * $-x, -y, -z$.

groups, and separation more than the free anionic value is indicative of a unidentate ligand.[14] Therefore the absorption peak at 1676 $cm^{-1}$ is attributed to the asymmetric monodentate carboxylato ligands and bands at 1614 and 1401 $cm^{-1}$ for the complex are assigned to O–C–O asymmetric and symmetric stretching vibrations of bridging carboxylato ligands, respectively.

Thermogravimetric analysis for the complex indicates that the complex loses two lattice water molecules at *ca.* 80°C followed by the eight-coordinated water molecules with a weight loss of 11.40% being close to the calculated value of 10.78%. The resulting residue is unstable and its organic moieties continue to decompose to *ca.* 210°C with a weight loss of 37.17%

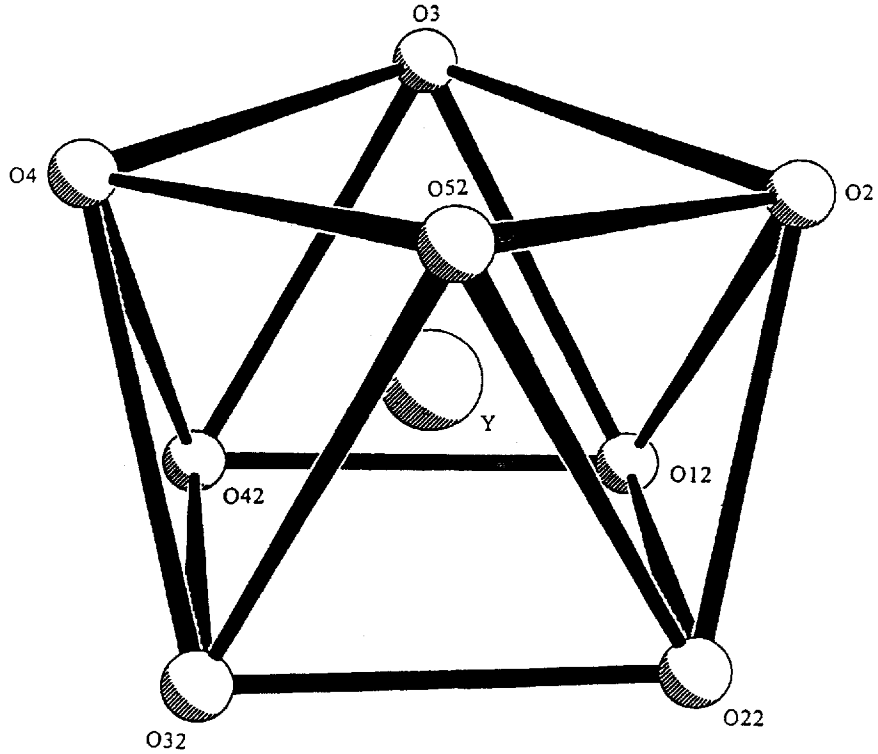


FIGURE 2 The double-capped triprismatic coordination geometry of the Y atom.

which is somewhat smaller than that required for the $CH_2COO$ moiety (41.67%). This value suggests that almost all the organic moieties have decomposed and the residue is mainly ($2YCl_3 + CuCl_2$) at *ca.* 350°C. At higher temperatures $CuCl_2$ is released from the residue to 580°C with a weight loss of *ca.* 29.58%, comparable with the calculated value of 30.51%. The final residue is $YCl_3$.

### *Acknowledgements*

The work is supported by the Science Foundation of the Shanghai Education Commission and Shanghai Jiaotong University. We thank Prof. G. Ferguson at the Department of Chemistry and Biochemistry, University of Guelph, Canada, for the treatment of the disordered moieties of the chloroacetato ligand.

## *References*

[1] O. Kahn, *Molecular Magnetism* (VCH Verlagsgesellschaft, Weinheim, Germany, 1993).
[2] O. Kahn, *Struct. Bonding*, **67**, 89 (1987).
[3] A. Gleizes and M. Verdaguer, *J. Am. Chem. Soc.*, **103**, 7373 (1981).
[4] U. Bossek, T. Weyhermuller, K. Weighardt, B. Nuber and J. Weiss, *J. Am. Chem. Soc.*, **112**, 6387 (1990).
[5] Y. Naruta, M. Sasayama and T. Sasaki, *Angew. Chem., Int. Ed. Engl.*, **33**, 1839 (1994).
[6] R. George, O. Kahn and O. Guillou, *Phys. Rev.*, **49**, 3235 (1994).
[7] Y. Sunatsuki, M. Nakamura, N. Matsumoto and F. Kai, *Bull. Chem. Soc. Jpn.*, **70**, 1851 (1997).
[8] R.D. Cannon and R.P. White, *Prog. Inorg. Chem.*, **36**, 195 (1988).
[9] T. Tanase, S.P. Watton and S.J. Lippard, *J. Am. Chem. Soc.*, **116**, 9401 (1994).
[10] W. Clegg, I.R. Little and B.P. Strauhan, *J. Chem. Soc., Dalton Trans.*, 1916 (1988).
[11] G.M. Sheldrick, SHELXS 97. Program for the Solution of Crystal Structures, University of Göttingen, Germany 1990.
[12] G.M. Sheldrick, SHELXL 97. Program for the Solution of Crystal Structures, University of Göttingen, Germany 1997.
[13] Siemens XP. Molecular Graphics Program, Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA 1990.
[14] G.B. Deacon and R.J. Phillips, *Coord. Chem. Rev.*, **33**, 227 (1980).