Stomberg, R. & Olson, S. (1984*a*). *Acta Chem. Scand. Ser. A*, **38**, 801–806.

Stomberg, R. & Olson, S. (1984*b*). *Acta Chem. Scand. Ser. A*, **38**, 821–823.

Stomberg, R., Olson, S. & Svensson, I. B. (1984). *Acta Chem. Scand. Ser. A*, **38**, 653–656.

Szentivanyi, H. & Stomberg, R. (1984). *Acta Chem. Scand. Ser. A*, **38**, 101–107.

Acta Cryst. (1990). C**46**, 741–745

A Coordinated Carboxylic and Carboxylate Group in Two Cu^{2+} Complexes with a Mono-*N*-functionalized Tetraaza Macrocycle

By Martin Studer, Andreas Riesen and Thomas A. Kaden

Institute of Inorganic Chemistry of Basel, CH-4056 Basel, Switzerland

(*Received* 20 *February* 1989; *accepted* 9 *May* 1989)

Abstract. Bis{[2-(1,4,8,11-tetraazacyclotetradecylmethyl)benzoato-*N*,*N*′,*N*″,*N*‴,*O*]copper(II)} diperchlorate pentahydrate, (I); $[Cu_2(C_{18}H_{29}N_4O_2)_2](ClO_4)_2.5H_2O$, M_r = 1082·967, monoclinic, $P2_1$, a = 9·191 (3), b = 23·776 (3), c = 10·865 (4) Å, β = 101·32 (4)°, V = 2328·1 Å^3, Z = 4, D_x = 1·545 Mg m^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, μ = 1·043 mm^{-1}, F(000) = 1136, T = 298 K, R = 0·061 for 3918 reflections with $I \geq 2\sigma(I)$. {[2-(1,4,8,11-tetraazacyclotetradecylmethyl)benzoic acid-*N*,*N*′,*N*″,*N*‴,*O*]copper(II)} diperchlorate monohydrate (II); $[Cu(C_{18}H_{30}N_4O_2)](ClO_4)_2.H_2O$, M_r = 614·921, monoclinic, $P2_1/c$, a = 11·913 (3), b = 9·435 (2), c = 22·584 (4) Å, β = 90·12 (2)°, V = 2538·4 Å^3, Z = 4, D_x = 1·610 Mg m^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, μ = 1·066 mm^{-1}, F(000) = 1276, T = 298 K, R = 0·075 for 2750 reflections with $I \geq 3\sigma(I)$. In (I) and (II), the Cu^{2+} ion is surrounded by four N and one O donor in a distorted square pyramidal geometry. The macrocyclic nitrogens form the base plane and the oxygen, stemming from the carboxylate and carboxylic acid group in (I) and (II) respectively, is in the apical position. In both cases, the macrocycles are in the *trans*-III configuration and the Cu^{2+} ion is displaced by 0·18 and 0·11 Å from the best plane of the four N atoms, respectively.

Introduction. There is a growing interest in functionalized macrocycles and their metal complexes (Busch, 1978; Kaden, 1984), because of the exceptional thermodynamic and kinetic properties of these compounds. Monosubstituted macrocycles, although difficult to obtain, are of particular interest since they allow the study of the influence of an additional donor group on the properties of an already coordinated metal ion. As described earlier (Studer & Kaden, 1986), we developed a one-step synthesis for mono-*N*-functionalized macrocycles carrying a carboxylic group in the side chain. The observation that the Cu^{2+} complex of 2-(1,4,8,11-tetraazacyclotetradecylmethyl)benzoic acid (*L*H, Fig. 1) shows a pH dependent equilibrium between a protonated uncoordinated and a deprotonated coordinated side chain in solution (Studer & Kaden, 1986) induced us to study the nature of these complexes, especially in view of the effect of the protonation state of the side chain on the coordination to the Cu^{2+}. We isolated crystals of both the protonated and the deprotonated forms of this complex and solved their structure by X-ray diffraction analysis.

Experimental. The synthesis of *L*H has been described previously (Studer & Kaden, 1986). Crystals of (I) can be isolated by adjusting the pH of the mother liquor of (II) (see below) to 8–9 and slowly evaporating the solvent. Analytical calculation for $[Cu_2(C_{18}H_{29}N_4O_2)_2](ClO_4)_2.5H_2O$ (1082·967): C 39·92, H 6·33, Cl 6·55, Cu 11·73, N 10·35, H_2O 8·32%. Found: C 40·14, H 6·05, Cl 6·55, Cu 11·8, N 10·39, H_2O 8·39%. IR(KBr): 1600, 1580

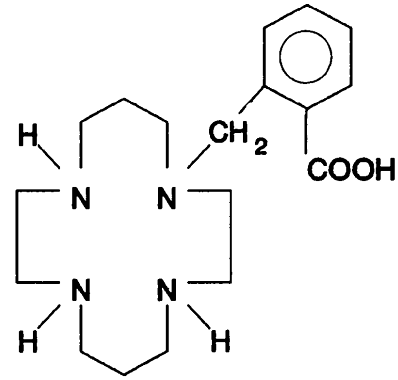

Fig. 1. The macrocyclic ligand *L*H.

0108-2701/90/050741-05$03.00

and 1550 cm^{-1} (COO^-). Synthesis of (II). An equimolar solution of LH.4HCl and $CuCl_2$ is adjusted with 0·5 M NaOH to pH 7. After two hours, the mixture is filtered and 1 M $HClO_4$ is added to the filtrate until pH 1 is reached, when (II) precipitates. The mixture is then heated to 373 K and sufficient water is added that the precipitate redissolves. Crystals of (II) can be collected after cooling the hot solution very slowly. Analytical calculation for $[Cu(C_{18}H_{30}N_4O_2)](ClO_4)_2.H_2O$: C 35·16, H 5·25, N 9·11, Cl 11·53, Cu 10·33, H_2O 2·92%. Found: C 35·13, H 5·27, N 9·21, Cl 11·63, Cu 10·35, H_2O 3·44%. IR(KBr): 1680 cm^{-1} (COOH).

X-ray data collection for (I) and (II). An Enraf–Nonius CAD-4 diffractometer controlled by a Digital MicroVAX computer was used for measurements, with Mo $K\alpha$ radiation monochromated by graphite.

Compound (I). Cell parameters were obtained from crystals of size 0·1 × 0·2 × 0·2 mm by least-squares procedure on 25 strong reflections in the 2θ range 12–27°. 5215 reflections ($2 \leq \theta \leq 27°$) were measured in the range $-11 \leq h \leq 11, 0 \leq k \leq 30, 0 \leq l \leq 13$ by ω–2θ scan technique. No significant variation in the intensities of three standards (1,11,1; $31\bar{2}$; $41\bar{3}$) monitored every 3600 s was observed. 3918 reflections observed [$I > 2\sigma(I)$], 4521 unique, R_{int} = 0·061. The raw data set was corrected for polarization effects, but no corrections for absorption were made. Positional parameters of the metal ion were determined by a three-dimensional Patterson map (*SHELXS*86; Sheldrick, 1986). The remaining atoms were localized by subsequent difference Fourier maps. Anisotropic thermal parameters for all non-H atoms and isotropic H atoms in calculated positions were refined in a blocked-matrix refinement on F with 588 parameters. wR = 0·061; $w = 0{\cdot}60/[\sigma^2(F) + 8{\cdot}85 \times 10^{-3} F^2]$. The maximum ratio of least-squares shift to e.s.d. was 0·1, and the largest positive peak on the ΔF map was 0·67, the largest negative peak −0·42 e $Å^{-3}$. Scattering factors for C, H, Cl, N, and O are given in *SHELX*76 (Sheldrick, 1976), and those for Cu^{II} are from Cromer & Mann (1968). Atomic parameters are given in Table 1,* selected bond lengths and angles in Table 2 and the numbering scheme is shown in Fig. 2.

Table 1. *Fractional atomic coordinates and* U_{eq} ($Å^2$) *values for* (I)

$U_{eq} = \frac{1}{3}\sum_i U_{ii} (\times 10^{-2})$.

	x	y	z	U_{eq}
Cu(1)	0·2479 (1)	0·5000	−0·0900 (1)	3·3
O(1)	0·3110 (8)	0·5895 (3)	−0·0910 (6)	4·6
N(1)	0·3301 (8)	0·4909 (3)	0·0944 (7)	3·6
N(2)	0·0427 (8)	0·4975 (4)	−0·0471 (7)	4·5
N(3)	0·1577 (8)	0·5008 (4)	−0·2754 (7)	4·2
N(4)	0·4405 (9)	0·4810 (3)	−0·1461 (7)	3·9
C(1)	0·2015 (10)	0·4731 (4)	0·1534 (8)	3·5
C(2)	0·0585 (10)	0·5014 (5)	0·0902 (8)	4·2
C(3)	−0·0664 (12)	0·5387 (6)	−0·1144 (11)	5·9
C(4)	−0·0922 (12)	0·5318 (7)	−0·2542 (11)	6·6
C(5)	0·0376 (13)	0·5435 (6)	−0·3138 (11)	5·7
C(6)	0·2822 (12)	0·5089 (5)	−0·3427 (9)	5·1
C(7)	0·4026 (12)	0·4696 (5)	−0·2813 (10)	5·0
C(8)	0·5406 (12)	0·4374 (5)	−0·0784 (10)	5·3
C(9)	0·5774 (12)	0·4489 (5)	0·0611 (11)	5·3
C(10)	0·4429 (11)	0·4438 (4)	0·1249 (10)	4·4
C(11)	0·4031 (11)	0·5432 (4)	0·1547 (9)	3·9
C(12)	0·2983 (10)	0·5900 (4)	0·1781 (9)	3·4
C(13)	0·2623 (11)	0·5937 (4)	0·2956 (9)	3·9
C(14)	0·1654 (12)	0·6340 (5)	0·3232 (10)	5·2
C(15)	0·1062 (11)	0·6726 (5)	0·2325 (10)	4·7
C(16)	0·1466 (10)	0·6725 (4)	0·1161 (9)	3·9
C(17)	0·2439 (9)	0·6309 (4)	0·0887 (9)	3·4
C(18)	0·2871 (10)	0·6344 (4)	−0·0370 (9)	3·5
O(2)	0·2935 (9)	0·6813 (3)	−0·0865 (7)	5·3
Cu(2)	0·3731 (1)	0·2674 (1)	0·4309 (1)	3·6
O(3)	0·4250 (10)	0·1746 (3)	0·4276 (7)	5·7
N(5)	0·4458 (8)	0·2738 (4)	0·6196 (7)	3·8
N(6)	0·1647 (8)	0·2717 (4)	0·4667 (7)	3·8
N(7)	0·2937 (10)	0·2682 (4)	0·2452 (8)	4·9
N(8)	0·5751 (10)	0·2799 (3)	0·3843 (9)	4·8
C(19)	0·3152 (12)	0·2929 (5)	0·6705 (11)	5·4
C(20)	0·1735 (10)	0·2660 (6)	0·6019 (10)	5·0
C(21)	0·0548 (12)	0·2316 (5)	0·3922 (13)	5·7
C(22)	0·0357 (14)	0·2417 (6)	0·2524 (13)	6·7
C(23)	0·1720 (14)	0·2283 (6)	0·1986 (13)	6·4
C(24)	0·4228 (14)	0·2600 (5)	0·1840 (11)	6·2
C(25)	0·5468 (14)	0·2935 (5)	0·2521 (13)	6·5
C(26)	0·6784 (13)	0·3204 (5)	0·4613 (13)	6·2
C(27)	0·6988 (13)	0·3083 (5)	0·5966 (13)	5·8
C(28)	0·5651 (13)	0·3172 (5)	0·6514 (12)	5·1
C(29)	0·5106 (10)	0·2197 (4)	0·6806 (10)	3·7
C(30)	0·4026 (10)	0·1733 (4)	0·6945 (9)	3·6
C(31)	0·3590 (13)	0·1695 (5)	0·8123 (10)	5·1
C(32)	0·2625 (14)	0·1266 (6)	0·8352 (12)	6·4
C(33)	0·2115 (12)	0·0891 (5)	0·7428 (11)	5·3
C(34)	0·2580 (11)	0·0901 (5)	0·6294 (10)	4·5
C(35)	0·3528 (10)	0·1328 (4)	0·6042 (9)	3·4
C(36)	0·4043 (10)	0·1300 (4)	0·4808 (9)	3·3
O(4)	0·4247 (9)	0·0833 (3)	0·4371 (7)	5·2
Cl(1)	−0·0475 (3)	0·4292 (1)	0·4078 (3)	5·1
O(5)	0·0390 (12)	0·4774 (4)	0·3929 (10)	8·4
O(6)	−0·1906 (14)	0·4366 (7)	0·3377 (17)	14·3
O(7)	0·0002 (21)	0·3844 (7)	0·3505 (22)	18·6
O(8)	−0·0568 (27)	0·4215 (9)	0·5213 (12)	22·6
Cl(2)	0·0655 (4)	0·3459 (1)	0·9116 (3)	6·3
O(9)	0·0398 (20)	0·2931 (5)	0·8646 (14)	15·0
O(10)	0·1406 (24)	0·3794 (5)	0·8492 (18)	23·0
O(11)	−0·0541 (20)	0·3722 (8)	0·9320 (29)	24·8
O(12)	0·1427 (26)	0·3450 (7)	1·0317 (17)	19·0
OW(1)	−0·4080 (9)	0·5928 (4)	−0·1700 (8)	5·7
OW(2)	0·7158 (9)	0·1686 (4)	0·3501 (8)	5·5
OW(3)	0·5511 (9)	0·4759 (3)	0·4618 (8)	5·7
OW(4)	0·6769 (14)	0·2929 (5)	0·9828 (11)	10·3
OW(5)	0·3409 (8)	0·3876 (4)	0·4172 (10)	7·2

Compound (II). Cell parameters were obtained from crystals of size 0·1 × 0·2 × 0·3 mm by least-squares procedure on 25 strong reflections in the 2θ range 5–29°. 2750 reflections ($2 \leq \theta \leq 27°$) were measured in the range $-15 \leq h \leq 15, 0 \leq k \leq 12, 0 \leq l \leq 28$ by ω–2θ scan technique. No significant variation in the intensities of four standards ($3\bar{1}\bar{4}$; $5\bar{1}\bar{6}$; $20\bar{8}$; $2\bar{3}\bar{3}$) monitored every 3600 s was observed. 2750 reflections observed [$I > 3\sigma(I)$], 4025 unique, R_{int} = 0·076. The raw data set was corrected for polarization effects, but no corrections for absorption were made. Positional parameters of the metal ion were determined by a three-dimensional Patterson map

---

* Lists of structure factors, anisotropic thermal parameters, bond lengths and angles and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52500 (52 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Selected bond distances* (Å) *and angles* (°) *for* (I)

Cu(1)—N(1)	2·010 (7)	Cu(2)—N(5)	2·033 (8)
Cu(1)—N(2)	2·031 (8)	Cu(2)—N(6)	2·030 (8)
Cu(1)—N(3)	2·022 (7)	Cu(2)—N(7)	2·007 (8)
Cu(1)—N(4)	2·032 (9)	Cu(2)—N(8)	2·040 (8)
Cu(1)—O(1)	2·206 (7)	Cu(2)—O(3)	2·261 (8)
Cu(1)—O(10)	3·062 (13)	Cu(2)—OW(5)	2·874 (9)
C(18)—O(1)	1·258 (12)	C(36)—O(3)	1·240 (13)
C(18)—O(2)	1·244 (12)	C(36)—O(4)	1·236 (12)
N(1)—Cu(1)—N(2)	87·2 (3)	N(5)—Cu(2)—N(6)	86·5 (3)
N(1)—Cu(1)—N(3)	174·0 (3)	N(5)—Cu(2)—N(7)	174·8 (4)
N(1)—Cu(1)—N(4)	95·5 (3)	N(5)—Cu(2)—N(8)	96·0 (3)
N(2)—Cu(1)—N(3)	90·6 (3)	N(6)—Cu(2)—N(7)	91·3 (3)
N(2)—Cu(1)—N(4)	164·8 (4)	N(6)—Cu(2)—N(8)	168·3 (3)
N(3)—Cu(1)—N(4)	85·1 (3)	N(7)—Cu(2)—N(8)	85·3 (4)
N(1)—Cu(1)—O(1)	93·5 (3)	N(5)—Cu(2)—O(3)	93·4 (3)
N(2)—Cu(1)—O(1)	106·3 (3)	N(6)—Cu(2)—O(3)	105·2 (3)
N(3)—Cu(1)—O(1)	92·5 (3)	N(7)—Cu(2)—O(3)	91·7 (3)
N(4)—Cu(1)—O(1)	88·2 (3)	N(8)—Cu(2)—O(3)	86·2 (3)
O(1)—Cu(1)—O(10)	167·4 (3)	O(3)—Cu(2)—OW(5)	172·0 (3)
O(1)—C(18)—O(2)	122·1 (9)	O(3)—C(36)—O(4)	122·6 (10)

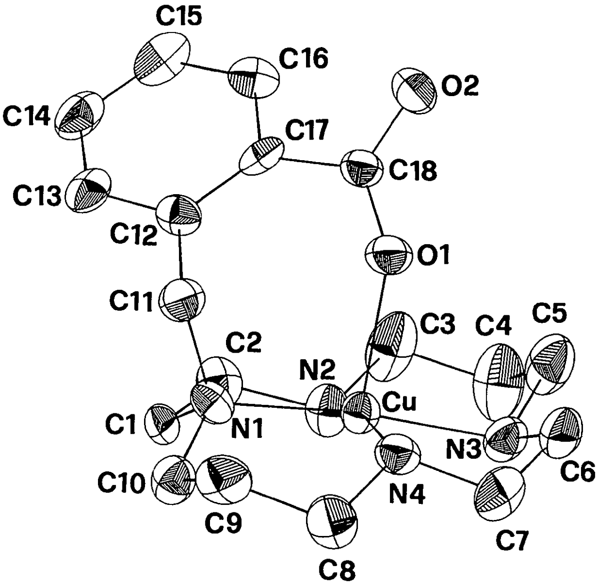

Fig. 2. *ORTEP* (Johnson, 1965) plot of (I).

(*SHELXS*86; Sheldrick 1986). The remaining atoms were localized by subsequent difference Fourier maps. Anisotropic thermal parameters for all non-H atoms and isotropic H atoms in calculated positions were refined in a full-matrix refinement on F with 361 parameters. $wR = 0{\cdot}075$; $w = 1{\cdot}78/[\sigma^2(F) + 2{\cdot}26 \times 10^{-3}F^2]$. The maximum ratio of least-squares shift to e.s.d. was 0·02, and the largest positive peak on the ΔF map was 0·82 e Å^{-3}, the largest negative peak $-$ 0·50 e Å^{-3}. Scattering factors for C, H, Cl, N and O are given in *SHELX*76 (Sheldrick, 1976), and those for Cu$^{\mathrm{II}}$ are from Cromer & Mann (1968). Atomic parameters are given in Table 3, selected bond lengths and angles in Table 4 and the numbering scheme is shown in Fig. 3.

Table 3. *Fractional atomic coordinates and* U_{eq} (Å^2) *values for* (II)

$$U_{\mathrm{eq}} = \tfrac{1}{3}\textstyle\sum_i U_{ii} (\times 10^{-2}).$$

	x	y	z	k	U_{eq}
Cu	0·2208 (1)	0·2035 (1)	0·1305 (1)	1·0	4·1
O(1)	0·2968 (5)	0·4201 (6)	0·1440 (2)	1·0	5·8
N(1)	0·2719 (6)	0·1304 (7)	0·2108 (3)	1·0	5·5
N(2)	0·0677 (6)	0·2283 (8)	0·1674 (3)	1·0	5·5
N(3)	0·1635 (6)	0·2640 (7)	0·0500 (3)	1·0	5·0
N(4)	0·3640 (6)	0·1529 (8)	0·0868 (4)	1·0	6·6
C(1)	0·1680 (9)	0·1021 (11)	0·2455 (4)	1·0	7·2
C(2)	0·0805 (8)	0·2126 (12)	0·2331 (4)	1·0	7·1
C(3)	0·0051 (8)	0·3555 (11)	0·1515 (5)	1·0	7·2
C(4)	−0·0130 (9)	0·3661 (12)	0·0855 (5)	1·0	7·9
C(5)	0·0895 (8)	0·3918 (11)	0·0497 (4)	1·0	7·1
C(6)	0·2631 (8)	0·2876 (10)	0·0128 (4)	1·0	6·2
C(7)	0·3418 (9)	0·1677 (11)	0·0220 (4)	1·0	7·3
C(8)	0·4177 (9)	0·0186 (12)	0·1008 (6)	1·0	9·5
C(9)	0·4376 (10)	−0·0021 (11)	0·1658 (6)	1·0	9·1
C(10)	0·3315 (9)	−0·0094 (9)	0·2030 (4)	1·0	7·1
C(11)	0·3537 (7)	0·2284 (9)	0·2425 (4)	1·0	5·8
C(12)	0·3030 (7)	0·3564 (9)	0·2732 (4)	1·0	5·6
C(13)	0·2782 (9)	0·3478 (13)	0·3326 (4)	1·0	7·3
C(14)	0·2425 (10)	0·4639 (15)	0·3645 (5)	1·0	8·8
C(15)	0·2317 (9)	0·5948 (13)	0·3378 (5)	1·0	7·9
C(16)	0·2585 (8)	0·6055 (10)	0·2789 (5)	1·0	7·1
C(17)	0·2932 (7)	0·4895 (9)	0·2457 (4)	1·0	5·4
C(18)	0·3134 (7)	0·5092 (9)	0·1819 (4)	1·0	5·2
O(2)	0·3522 (7)	0·6356 (7)	0·1690 (3)	1·0	8·1
Cl(1)	0·6155 (2)	0·0759 (4)	0·6029 (1)	1·0	8·4
O(11)	0·5638 (8)	0·1320 (15)	0·6511 (5)	1·0	17·0
O(12)	0·7191 (7)	0·0446 (15)	0·6154 (7)	1·0	18·0
O(13)	0·5832 (25)	−0·0772 (22)	0·6055 (16)	0·5	17·6
O(14)	0·5624 (18)	0·0134 (49)	0·5597 (14)	0·5	18·2
O(15)	0·5578 (33)	0·1367 (52)	0·5637 (12)	0·5	24·8
O(16)	0·6889 (34)	0·1763 (39)	0·5658 (10)	0·5	19·3
Cl(2)	0·0667 (3)	−0·1577 (4)	0·0877 (2)	1·0	10·6

Table 4. *Selected bond distances* (Å) *and angles* (°) *for* (II)

Cu—N(1)	2·033 (7)	C(18)—O(1)	1·216 (9)
Cu—N(2)	2·020 (7)	C(18)—O(2)	1·312 (10)
Cu—N(3)	2·022 (7)	OW(1)—O(2)	2·583 (7)
Cu—N(4)	2·030 (7)		
Cu—O(1)	2·256 (5)		
Cu—O(21)	2·786 (16)		
N(1)—Cu—N(2)	86·6 (3)	N(1)—Cu—O(1)	93·9 (2)
N(1)—Cu—N(3)	176·1 (3)	N(2)—Cu—O(1)	101·6 (3)
N(1)—Cu—N(4)	95·9 (3)	N(3)—Cu—O(1)	90·0 (2)
N(2)—Cu—N(3)	92·0 (3)	N(4)—Cu—O(1)	86·6 (3)
N(2)—Cu—N(4)	171·2 (3)	O(1)—Cu—O(21)	170·0 (3)
N(3)—Cu—N(4)	85·0 (3)	O(1)—C(18)—O(2)	121·8 (8)

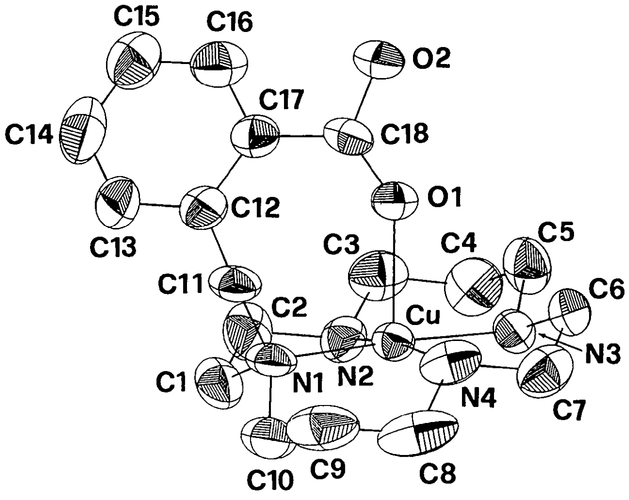

Fig. 3. *ORTEP* (Johnson, 1965) plot of (II).

Discussion. As expected from the conditions of the syntheses and the potentiometric results (Studer & Kaden, 1986), (I) contains the CuL^+ unit with a carboxylate and (II) the $CuLH^{2+}$ unit with a carboxylic acid group. In contrast to measurements in solution, where a shift in the absorption maximum is observed on changing the pH from alkaline to acidic conditions, thus indicating a significant structural change, there are only small differences between CuL^+ and $CuLH^{2+}$ in the solid state. Within the limits of experimental error, the bond lengths and angles in (I) and (II) are the same [mean Cu—N bond 2·025 (9) Å, mean Cu—O bond 2·24 (3) Å]. In both cases the macrocycle is in the *trans*-III configuration according to the nomenclature of Bosnich, Poon & Tobe (1965). The Cu^{2+} ion is square pyramidally coordinated by four nearly coplanar N and an axial O atom. The distance of the metal ion to the best plane through the four nitrogens is 0·18 and 0·11 Å, respectively. The fact that in (I) the O atom in the apical position originates from a carboxylate and in (II) from a carboxylic acid group seems to have little influence on the coordination sphere of the Cu^{2+} ion.

The only significant difference between the CuL^+ and the $CuLH^{2+}$ units is found between the carboxylate and the carboxylic acid groups. In (I), the C—O bonds are very similar to each other [C(18)—O(1), C(18)—O(2) 1·258 (12), 1·244 (12) Å and C(36)—O(3), C(36)—O(4) 1·240 (13), 1·236 (12) Å], as expected for a carboxylate group. In contrast, (II) shows two distinctly different C—O bonds with 1·216 (9) for C(18)—O(1) and 1·312 (10) Å for C(18)—O(3), the shorter belonging to the coordinated O atom. The distance between O(2) and the water molecule OW(1) is 2·583 Å, indicating that the carboxylic proton forms a hydrogen bond to the water.

The asymmetric unit of (I) contains two crystallographically different CuL^+ units, two perchlorate ions and five water molecules. Although (I) crystallizes from a racemic mixture and contains both enantiomers, the space group is the optically active $P2_1$. There is no possibility of transforming this group into one with a higher symmetry. The hypothetical 'centre of symmetry' in the position $x = 0·56$, $y = 0·13$, $z = 0·26$ is destroyed by small differences in the surroundings of the two Cu^{2+} ions: Cu(1) has a long bond (3·093 Å) to O(10) of a ClO_4^- ion, whereas Cu(2) has one (2·874 Å) to OW(5) of a water molecule (Fig. 4).

It is difficult to compare (I) and (II) with other compounds, since a search of the literature reveals no similar five-coordinated macrocyclic Cu^{2+} complex. The $Cu—N_4$ unit closely resembles that found in the Cu^{2+} complex of [14]aneN_4 with the *trans*-III configuration (Tasker & Sklar, 1975). Tschudin, Riesen & Kaden (1989) describe a pentacoordinate Cu^{2+} complex of 1-[2(ethoxycarbonyl)ethyl]-4,8,11-trimethyl-1,4,8,11-tetraazacylotetradecane with an ester group axially coordinated to Cu^{2+}. The Cu—O bond (2·22 Å) is similar to those of (I) and (II). However, the macrocycle of this compound is in the *trans*-I configuration (Bosnich, Poon & Tobe, 1965) and the square pyramid is considerably distorted towards a trigonal bipyramidal geometry. The Ni^{2+} complex of 1-carboxymethyl-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane (Xu, Ni & Lin, 1988), and the Cu^{2+} complexes of 1,8-bis(carboxymethyl)-1,4,8,11-tetraazacyclotetradecane (Helps, Parker, Chapman & Ferguson, 1988) and of 1,4,8,11-tetrakis(carboxymethyl)-1,4,8,11-tetraazacyclotetradecane (Riesen, Zehnder & Kaden, 1988) have metal ions in a distorted octahedral arrangement and cannot be used for discussing the coordination geometry. However, they all have coordinated carboxylate groups. As in (I), the Cu—O bonds are between 2·20 and 2·26 Å and the C—O bonds of the carboxylate group range from 1·23 to 1·26 Å.

It is interesting to note that in one crystallization batch we obtained another form of (II) which has been partially studied by X-ray diffraction. The unit-cell parameters are $a = 8·599$ (1), $b = 9·092$ (4), $c =$

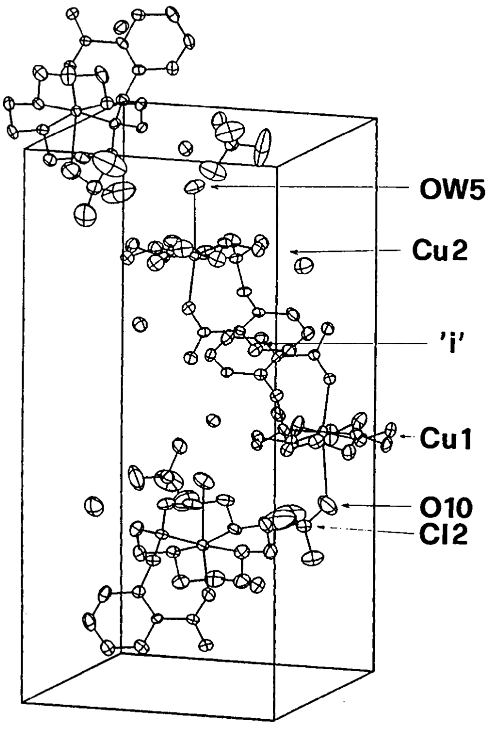

Fig. 4. Unit cell of (II), showing the hypothetical inversion centre 'i' and the small differences between the 'enantiomeric' complexes Cu(1) and Cu(2).

15·198 (2) Å, α = 92·14 (2), β = 95·04 (1), γ = 98·78 (2)°. The structure is very similar to the one discussed above with a Cu^{2+} pentacoordinated by four N and one O donor, but there is no water molecule in this compound. No further work on this form is planned.

The support of this work by the Swiss National Science Foundation (Project N. 2000-5.372) is gratefully acknowledged.

References

Bosnich, B., Poon, C. K. & Tobe, M. L. (1965). *Inorg. Chem.* **4**, 1102–1108.

Busch, D. H. (1978). *Acc. Chem. Res.* **11**, 392–400.

Cromer, D. T. & Mann, J. B. (1968). *Acta Cryst.* A**24**, 321–324.

Helps, I. M., Parker, D., Chapman, J. & Ferguson G. (1988). *J. Chem. Soc. Chem. Commun.* pp. 1094–1095.

Johnson, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee, USA.

Kaden, Th. A. (1984). *Top. Curr. Chem.* **121**, 157–179.

Riesen, A., Zehnder, M. & Kaden, Th. A. (1988). *Acta Cryst.* C**44**, 1740–1742.

Sheldrick, G. M. (1976). *SHELX76*. Program for crystal structure determination, Univ. of Cambridge, England.

Sheldrick, G. M. (1986). *SHELXS86*. Program for crystal structure solution. Univ. of Göttingen, Federal Republic of Germany.

Studer, M. & Kaden, Th. A. (1986). *Helv. Chim. Acta*, **69**, 2081–2086.

Tasker, P. A. & Sklar, L. J. (1975). *Cryst. Mol. Struct.* **5**, 329–343.

Tschudin, D. Riesen, A. & Kaden Th. A. (1989). *Helv. Chim. Acta*, **72**, 131–138.

Xu J. D., Ni S. H. & Lin Y. J. (1988). *Inorg. Chem.* **27**, 4651–4657.

Acta Cryst. (1990). C**46**, 745–747

Structure of Bis(η-pentamethylcyclopentadienyl)chromium(III) Iodide, $[Cr(C_5Me_5)_2]I$

By James Darkwa,* John F. Richardson† and Ted S. Sorensen

Department of Chemistry, University of Calgary, Calgary, Alberta, Canada T2N 1N4

(*Received* 10 *May* 1989; *accepted* 28 *July* 1989)

Abstract. $C_{20}H_{30}Cr^+.I^-$, M_r = 449·36, triclinic, $P\bar{1}$, a = 10·414 (3), b = 11·721 (3), c = 8·710 (3) Å, α = 100·96 (2), β = 98·99 (2), γ = 80·89 (2)°, V = 1021·8 Å^3, Z = 2, D_x = 1·46 Mg m^{-3}, Mo $K\alpha$, λ = 0·7107 Å, μ = 2·04 mm^{-1}, $F(000)$ = 454, T = 294 K, final R = 0·036 for 2136 reflections. The structure consists of a cationic moiety, in which a Cr atom is sandwiched between two C_5Me_5 rings, and an iodide counter ion. The rings are planar to within 0·05 Å and are slightly rotated from an ideal eclipsed position by 6·6°. The Cr—ring-centroid distances are 1·863 (5) and 1·858 (5) Å.

Introduction. The reaction of chromocene with halides and alkyl halides produces the chromocenium cation (Fischer, Ulm & Kuzel, 1963; Kohler, de Cao, Ackermann & Seldlmair, 1983). The cationic species have so far only been characterized by elemental analysis and by paramagnetic ^1H and ^{13}C NMR spectroscopy. Based on these analyses, the structure of the chromocenium cation in these salts is assumed to have the sandwiched structure characteristic of metallocenes.

In our effort to generate and isolate R_3Si^+ we reacted $(C_5Me_5)_2Cr$ and R_3SiX (where R = Me, i-Pr and X = Cl, Br, I) with the hope that the decamethylchromocene would abstract the halide to form $[(C_5Me_5)_2CrI]^-$ and R_3Si^+. The solid products obtained, though ionic, had no silicon present as evidenced by ^{29}Si NMR and the reactions appeared to have followed the course of Fischer's reaction described above. An X-ray structural analysis of the iodide analogue was carried out to determine the structure of the decamethylchromocene cation. The results of our study are reported herein.

Experimental. Bis(pentamethylcyclopentadienyl)-chromium(III) iodide was prepared by the reaction of $(C_5Me_5)_2Cr$ and degassed Me_3SiI in tetrahydrofuran under an argon atmopshere. Crystals suitable for X-ray analysis were obtained by slow diffusion of hexane into a CH_2Cl_2 solution of the compound (caution: the product decomposes in chlorinated solvents over a period of one week). The highly air- and moisture-sensitive crystals were mounted in glass capillaries by using a glovebox with an inert N_2 atmosphere.

Orange cut plate, 0·14 × 0·32 × 0·43 mm; Enraf–Nonius CAD-4F diffractometer, graphite-monochromated Mo $K\alpha$ radiation; lattice parameters

---

* Present address: Department of Chemistry, University of Zimbabwe, PO Box MP167, Mount Pleasant, Harare, Zimbabwe.

† Present address: Department of Chemistry, University of Louisville, Louisville, Kentucky, USA 40292.

0108-2701/90/050745-03$03.00