Fig. 2. Space-filling representation of $[\text{HgI}_2 \cdot 18\text{C}6]$.

macrocyclic ring, *i.e.* they have rotaxane-like structures. Of particular note are the closely related 18C6 complexes (Paige & Richardson, 1984; Kawasaki & Matsuura, 1984) with CdCl_2 and HgCl_2 , and the DA18C6 complex (Malmsten, 1979) with HgI_2 , where the gross structural features of the 1:1 complexes are analogous to that of $[\text{HgI}_2 \cdot 18\text{C}6]$. The present structure provides another example of the relatively rare hexagonal-bipyramidal geometry. The Hg—I bond distances [2.622 (1) Å] are the same as those observed by Jeffrey & Vlasse (1967) in HgI_2 , but significantly shorter than the value of 2.680 (1) Å reported by Malmsten (1979) for $[\text{HgI}_2 \cdot \text{DA18C6}]$. The Hg...O distances and the I—Hg...O angles (Table 2) do not depart significantly from those reported (Paige & Richardson, 1984) for $[\text{HgCl}_2 \cdot 18\text{C}6]$. A consequence of the accommodation of a large Hg atom at the centre of the 18C6 macrocycle is an increase in the magnitude of the mean O—C—C—O torsional angle [75 (2)°], *c.f.* the ‘normal’ value of *ca* 65° (Goldberg, 1980).

Surprisingly, although the title complex as a whole has within statistical significance $\bar{3}$ symmetry and

adopts a very similar packing arrangement to that reported by Paige & Richardson (1984) for $[\text{HgCl}_2 \cdot 18\text{C}6]$ and $[\text{CdCl}_2 \cdot 18\text{C}6]$, the crystals are not rhombohedral. This may be a consequence of accommodating covalently larger I atoms in the structure in place of Cl atoms. In fact, the unit-cell parameters initially chosen by Paige & Richardson (1984) for a *C*-face-centred cell of $a = 10.44$, $b = 11.46$, $c = 7.75$ Å, and $\beta = 82.21^\circ$ are all different from the present *C*-face-centred cell.

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Structures of Dibromo[N,N'-bis(2-pyridylmethylene)-1,3-propanediamine]copper(II) (1) and Bromo[N,N'-bis(2-pyridylmethylene)-1,4-butanediamine]copper(II) Bromide (2)

BY AARNE PAJUNEN AND SEIJA PAJUNEN

Department of Inorganic Chemistry, University of Helsinki, Vuorikatu 20, SF-00100 Helsinki 10, Finland

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Abstract. (1): $[\text{CuBr}_2(\text{C}_{15}\text{H}_{16}\text{N}_4)]$, $M_r = 475.7$, monoclinic, $C2/c$, $a = 13.286$ (3), $b = 9.723$ (3), $c = 13.234$ (2) Å, $\beta = 107.54$ (1)°, $V = 1630.1$ (5) Å³, $Z = 4$, $D_m = 1.94$ (3), $D_x = 1.94$ g cm⁻³, $\lambda(\text{Mo } \text{K}\alpha) =$

0.7107 Å, $\mu = 65.8$ cm⁻¹, $F(000) = 932$, $T = 293$ K, $R = 0.031$ for 1238 observed [$I > 2\sigma(I)$] of 1898 unique reflections. (2): $[\text{CuBr}(\text{C}_{16}\text{H}_{18}\text{N}_4)\text{Br}]$, $M_r = 489.8$, monoclinic, $P2_1/c$, $a = 12.142$ (3), $b =$

17.842 (5), $c = 8.770$ (4) Å, $\beta = 109.13$ (3)°, $V = 1795.0$ (8) Å³, $Z = 4$, $D_m = 1.81$, $D_x = 1.81$ Mg m⁻³, Mo $K\alpha$, $\mu = 59.8$ cm⁻¹, $F(000) = 964$, $T = 293$ K, $R = 0.064$ for 1842 observed [$I > 2\sigma(I)$] of 3374 unique reflections. (1) The Cu atom displays tetragonally distorted octahedral coordination. The coordination sphere is defined by the four N atoms of the ligand molecule in a planar arrangement and two bromide ions in the axial positions. The complex has a crystallographically required twofold axis. (2) The coordination geometry around Cu is slightly distorted trigonal bipyramidal with two N atoms and one bromide ion in equatorial and two N atoms in axial positions.

Introduction. Metal complexes formed by Cu^{II} and Schiff bases derived from ethylenediamine and 2-pyridinecarbaldehyde have been described by Goodwin & Lions (1960) in connection with their studies on quadridentate chelate compounds. To study the crystal structures of compounds containing fused chelate rings, we prepared complexes from CuBr₂ and Schiff bases containing ethylenediamine, 1,3-propanediamine or 1,4-butanediamine as the amino part and 2-pyridinecarbaldehyde as the carbonyl part. This paper describes the structure determination of complexes formed with the two latter Schiff bases.

Experimental. Preparation method of Goodwin & Lions (1960), recrystallization from methanol (1) or methanol–ethanol mixture (2). D_m by flotation in carbon tetrachloride/methyl iodide. Nicolet P3 four-circle diffractometer, Mo $K\alpha$ radiation, ω scan, variable scan speed, range 1.5–29.3° min⁻¹. Two standard reflections every 50 reflections, no significant variation. Empirical absorption correction (ψ scans). Experimental data and structure solution parameters are summarized in Table 1.

Structure solved by Patterson and Fourier methods (1) and direct methods (2) (MULTAN80; Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980), coordinates of H atoms calculated by geometrical considerations, confirmed by F synthesis showing only random fluctuations; full-matrix least-squares methods; H atoms fixed with $U = 0.06$ Å². Scattering factors for C, N, Cu and Br from Cromer & Mann (1968), for H from Stewart, Davidson & Simpson (1965); anomalous-dispersion corrections from *International Tables for X-ray Crystallography* (1974). Both structures are disordered; in (1), C(8) is disordered around the twofold rotation axis, in (2) the seven-membered ring is disordered and C(9) is divided between two positions with occupancy factors 0.7 and 0.3. XRAY76 (Stewart, Machin, Dickinson, Ammon, Heck & Flack, 1976) system of programs and PLUTO (Motherwell, 1976).

Table 1. *Experimental data and structure refinement parameters*

| | (1) | (2) |
|---------------------------------------------------------------------------|-----------------------------------------------------------------------------------------|------------------------------------------------|
| Crystal shape and size (mm) | Green prism 0.5 × 0.4 × 0.3 | Green needle 0.6 × 0.3 × 0.2 |
| Number of reflections | 14 | 15 |
| θ range (°) | 4 < θ < 12 | 6 < θ < 15 |
| Transmission factors | 1.0–0.72 | 1.0–0.66 |
| $(\sin\theta/\lambda)_{\text{max}}(\text{\AA}^{-1})$ | 0.649 | 0.594 |
| Range of h, k, l | 0 ≤ h ≤ 17 0 ≤ k ≤ 12 -17 ≤ l ≤ 17 | -14 ≤ h ≤ 14 0 ≤ k ≤ 21 0 ≤ l ≤ 10 |
| Standard reflections | 402; 111 | 040; 200 |
| Number of reflections measured | 2064 | 3495 |
| Number of unique reflections | 1898 | 3374 |
| R_{int} | 0.025 | 0.039 |
| Number of unobserved reflections $ I < 2\sigma(I)$ | 660 | 1532 |
| Number of H atoms located; total H | 16; 16 | 12; 18 |
| Number of parameters refined | 105 | 218 |
| Quantity minimized | $\sum w(F_o - F_c)^2$ $w = (a + F_o + B F_o ^2)^{-1}$ $a = 40.0; B = 0.008$ | $A = 80.0; B = 0.010$ |
| Final R ; wR | 0.031; 0.047 | 0.064; 0.090 |
| S | 0.230 | 0.229 |
| $(\Delta/\sigma)_{\text{max}}$ | 0.018 | 0.59 |
| $(\Delta\rho)_{\text{max}}, (\Delta\rho)_{\text{min}}(\text{e \AA}^{-3})$ | 0.27; -0.31 | 0.72; -0.85 |

Discussion. Final atomic coordinates and equivalent isotropic temperature factors are given in Tables 2 and 3. Bond lengths and angles in Tables 4 and 5.* Perspective views of (1) and (2) with atom numbering schemes are shown in Fig. 1.

The crystal structure of (1) consists of discrete monomeric tetragonally distorted octahedral Cu^{II} complexes. The coordination sphere is defined by four N atoms of the ligand molecule in almost planar arrangement and two bromide ions in axial positions. The four N atoms are coordinated, with distances Cu–N(imino) = 1.992 (4) and Cu–N(pyridine) = 2.034 (4) Å. Because of symmetry, Cu is exactly on the least-squares plane of the nitrogen atoms; N(1) and N(2) deviate 0.083 (5) and 0.072 (5) Å respectively from this plane. The angles subtended by the N atoms at Cu show significant deviations from 90°: N(1)–Cu–N(2) in the five-membered ring is 81.2 (2)° and N(1)–Cu–N(1)(-x, y, z) in the six-membered ring is 104.5 (2)°. Two bromide ions complete the coordination at a longer distance of 2.974 (1) Å.

The Cu atom lies on a crystallographic twofold axis and the symmetry of the complex molecule is C_2 . The terminal C atom of the six-membered ring is disordered around this axis and therefore the six-membered ring exists in the structure in two (chair and boat) conformations.

* Lists of structure factors, anisotropic thermal parameters and calculated hydrogen-atom positions have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42506 (18 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

In (2), the coordination can be described as trigonal bipyramidal. The Cu atom is surrounded by four N atoms of the ligand molecule and one bromide ion, located at the corners of a slightly distorted trigonal bipyramid. N(2), N(4) and Br(1) are in a plane, from which the Cu atom deviates by only 0.018 (5) Å. Atoms N(1), N(3) and Cu lie on a line, which makes an angle of 8.2 (5)° with the normal to this plane.

The angles formed by N and Cu atoms in the five-membered rings are significantly less than 90°: N(1)–Cu–N(2) is 81.3 (5) and N(3)–Cu–N(4) is 80.0 (4)°. This causes the trigonal bipyramidal coordination polyhedron to be distorted. The N(2)–Cu–N(3)

angle in the disordered seven-membered ring is 92.2 (5)°.

The trigonal-bipyramidal configuration can be considered as a distortion of the square-pyramidal arrangement through movement of the two *trans* N atoms [N(2) and N(4)] within the plane containing them and

Table 2. Final non-H-atom positional parameters ($\times 10^4$) and equivalent isotropic temperature factors ($\times 10^2$) for (1)

| | x | y | z | $U_{eq}(\text{Å}^2)$ |
|-------|------------|------------|------------|----------------------|
| Br | 1850.7 (4) | 1820.9 (6) | 1678.9 (4) | 4.07 (3) |
| Cu | 0 | 1894.1 (9) | 2500 | 5.02 (5) |
| N(1) | 749 (3) | 3175 (4) | 3708 (3) | 3.5 (2) |
| N(2) | 579 (3) | 489 (4) | 3620 (3) | 3.5 (2) |
| C(1) | 934 (5) | 4517 (6) | 3734 (4) | 3.1 (2) |
| C(2) | 1353 (5) | 5245 (6) | 4680 (4) | 3.9 (3) |
| C(3) | 1622 (4) | 4548 (6) | 5623 (4) | 4.2 (3) |
| C(4) | 1502 (4) | 3140 (6) | 5598 (4) | 4.7 (3) |
| C(5) | 1073 (4) | 2486 (5) | 4644 (3) | 4.8 (3) |
| C(6) | 974 (4) | 989 (5) | 4536 (4) | 3.2 (2) |
| C(7) | 504 (5) | -1010 (5) | 3483 (4) | 4.9 (6) |
| C(8)† | 400 (9) | -1438 (10) | 2388 (10) | 4.6 (6) |

† Population parameter 0.5.

Table 3. Final non-H-atom positional parameters ($\times 10^4$) and isotropic temperature factors ($\times 10^2$) for (2)

| | x | y | z | $U_{eq}(\text{Å}^2)$ |
|--------|-----------|-----------|------------|----------------------|
| Br(1) | 375 (1) | 3857 (1) | 2900 (2) | 6.1 (1) |
| Br(2) | -4038 (2) | 3533 (1) | 1774 (2) | 6.0 (1) |
| Cu | 1986 (1) | 4431 (1) | 2267 (2) | 3.7 (1) |
| N(1) | 1621 (9) | 5484 (5) | 2705 (12) | 3.4 (6) |
| N(2) | 2313 (10) | 4942 (6) | 388 (13) | 4.1 (7) |
| N(3) | 2597 (11) | 3458 (6) | 1798 (13) | 4.1 (6) |
| N(4) | 3501 (9) | 4321 (5) | 4376 (12) | 3.2 (6) |
| C(1) | 1324 (13) | 5751 (7) | 3924 (17) | 4.4 (8) |
| C(2) | 1262 (15) | 6506 (9) | 4250 (21) | 5.8 (10) |
| C(3) | 1542 (16) | 7005 (8) | 3253 (20) | 6.1 (10) |
| C(4) | 1797 (15) | 6748 (8) | 1907 (19) | 5.5 (10) |
| C(5) | 1846 (11) | 5983 (8) | 1688 (16) | 3.9 (7) |
| C(6) | 2195 (11) | 5644 (8) | 390 (16) | 4.0 (8) |
| C(7) | 2784 (15) | 4582 (9) | -774 (19) | 5.9 (10) |
| C(8) | 1883 (17) | 4024 (10) | -1822 (21) | 7.0 (10) |
| C(9A)† | 1403 (19) | 3421 (13) | -1080 (28) | 5.4 (14) |
| C(9B)‡ | 2212 (42) | 3279 (32) | -1148 (55) | 5.1 (23) |
| C(10) | 2076 (17) | 2997 (9) | 365 (20) | 6.9 (11) |
| C(11) | 3491 (13) | 3216 (8) | 2864 (17) | 4.6 (8) |
| C(12) | 4005 (12) | 3653 (7) | 4384 (18) | 4.3 (8) |
| C(13) | 4835 (13) | 3363 (8) | 5677 (19) | 5.3 (9) |
| C(14) | 5153 (14) | 3766 (10) | 7129 (20) | 6.1 (10) |
| C(15) | 4701 (13) | 4479 (10) | 7113 (18) | 5.8 (10) |
| C(16) | 3877 (11) | 4740 (8) | 5727 (17) | 4.5 (8) |

† Population parameter 0.7.

‡ Population parameter 0.3.

Table 4. Bond lengths (Å) and angles (°) for (1)

| | | | |
|---------------------------|-----------|-----------------------------|------------|
| Cu–Br | 2.974 (1) | C(1)–C(2) | 1.399 (7) |
| Cu–N(1) | 2.034 (4) | C(2)–C(3) | 1.370 (8) |
| Cu–N(2) | 1.992 (4) | C(3)–C(4) | 1.378 (8) |
| N(1)–C(1) | 1.326 (7) | C(4)–C(5) | 1.375 (6) |
| N(1)–C(5) | 1.359 (6) | C(5)–C(6) | 1.465 (7) |
| N(2)–C(6) | 1.264 (6) | C(7)–C(8) | 1.474 (14) |
| N(2)–C(7) | 1.468 (6) | C(7)–C(8) | 1.453 (12) |
| Br–Cu–Br [†] | 177.3 (1) | N(1)–C(1)–C(2) | 122.8 (5) |
| Br–Cu–N(1) | 92.3 (1) | C(1)–C(2)–C(3) | 119.3 (5) |
| Br–Cu–N(2) | 94.5 (1) | C(2)–C(3)–C(4) | 118.3 (5) |
| Br–Cu–N(1) [†] | 89.4 (1) | C(3)–C(4)–C(5) | 119.7 (5) |
| Br–Cu–N(2) [†] | 83.6 (1) | N(1)–C(5)–C(4) | 122.6 (5) |
| N(1)–Cu–N(2) | 81.2 (2) | N(1)–C(5)–C(6) | 114.0 (4) |
| N(1)–Cu–N(1) [†] | 104.5 (2) | C(4)–C(5)–C(6) | 123.3 (4) |
| N(2)–Cu–N(2) [†] | 93.4 (2) | N(2)–C(6)–C(5) | 118.4 (2) |
| Cu–N(1)–C(1) | 131.7 (3) | C(6)–N(2)–C(7) | 119.6 (4) |
| Cu–N(1)–C(5) | 111.1 (3) | N(2)–C(7)–C(8) | 112.6 (5) |
| Cu–N(2)–C(6) | 113.9 (3) | N(2)–C(7)–C(8) [†] | 113.0 (5) |
| Cu–N(2)–C(7) | 126.3 (3) | C(7)–C(8)–C(7) [†] | 120.6 (9) |
| C(1)–N(1)–C(5) | 117.1 (4) | | |

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

Table 5. Bond lengths (Å) and angles (°) for (2)

| | | | |
|------------------|------------|-------------------|----------|
| Cu–Br(1) | 2.428 (2) | C(2)–C(3) | 1.37 (3) |
| Cu–N(1) | 1.996 (10) | C(3)–C(4) | 1.39 (3) |
| Cu–N(2) | 2.033 (13) | C(4)–C(5) | 1.38 (2) |
| Cu–N(3) | 1.983 (12) | C(5)–C(6) | 1.47 (2) |
| Cu–N(4) | 2.148 (9) | C(7)–C(8) | 1.54 (2) |
| N(1)–C(1) | 1.32 (2) | C(8)–C(9A) | 1.47 (3) |
| N(1)–C(5) | 1.35 (2) | C(8)–C(9B) | 1.46 (6) |
| N(2)–C(6) | 1.26 (2) | C(9A)–C(10) | 1.47 (3) |
| N(2)–C(7) | 1.47 (2) | C(9B)–C(10) | 1.48 (6) |
| N(3)–C(10) | 1.46 (2) | C(11)–C(12) | 1.49 (2) |
| N(3)–C(11) | 1.25 (2) | C(12)–C(13) | 1.35 (2) |
| N(4)–C(12) | 1.34 (2) | C(13)–C(14) | 1.40 (2) |
| N(4)–C(16) | 1.35 (2) | C(14)–C(15) | 1.38 (3) |
| C(1)–C(2) | 1.38 (2) | C(15)–C(16) | 1.38 (2) |
| Br(1)–Cu–N(1) | 96.1 (3) | C(1)–C(2)–C(3) | 117 (2) |
| Br(1)–Cu–N(2) | 139.5 (3) | C(2)–C(3)–C(4) | 120 (1) |
| Br(1)–Cu–N(3) | 93.6 (4) | C(3)–C(4)–C(5) | 118 (2) |
| Br(1)–Cu–N(4) | 106.9 (3) | N(1)–C(5)–C(4) | 122 (1) |
| N(1)–Cu–N(2) | 81.3 (5) | N(1)–C(5)–C(6) | 114 (1) |
| N(1)–Cu–N(3) | 170.2 (5) | C(4)–C(5)–C(6) | 123 (1) |
| N(1)–Cu–N(4) | 95.8 (4) | N(2)–C(6)–C(5) | 118 (1) |
| N(2)–Cu–N(3) | 92.2 (5) | N(2)–C(7)–C(8) | 110 (2) |
| N(2)–Cu–N(4) | 113.5 (4) | C(7)–C(8)–C(9A) | 121 (2) |
| N(3)–Cu–N(4) | 80.0 (4) | C(7)–C(8)–C(9B) | 108 (2) |
| Cu–N(1)–C(1) | 129.1 (9) | C(8)–C(9A)–C(10) | 125 (2) |
| Cu–N(1)–C(5) | 112.8 (9) | C(8)–C(9B)–C(10) | 125 (4) |
| C(1)–N(1)–C(5) | 117.6 (11) | N(3)–C(10)–C(9A) | 114 (1) |
| Cu–N(2)–C(6) | 113.1 (11) | N(3)–C(10)–C(9B) | 116 (2) |
| Cu–N(2)–C(7) | 126.1 (9) | N(3)–C(11)–C(12) | 119 (1) |
| C(6)–N(2)–C(7) | 120.4 (13) | N(4)–C(12)–C(11) | 114 (1) |
| Cu–N(3)–C(10) | 125.8 (9) | N(4)–C(12)–C(13) | 124 (1) |
| Cu–N(3)–C(11) | 116.0 (10) | C(11)–C(12)–C(13) | 122 (1) |
| C(10)–N(3)–C(11) | 118.2 (12) | C(12)–C(13)–C(14) | 118 (1) |
| Cu–N(4)–C(12) | 110.3 (8) | C(13)–C(14)–C(15) | 118 (1) |
| Cu–N(4)–C(16) | 130.9 (8) | C(14)–C(15)–C(16) | 119 (1) |
| C(12)–N(4)–C(16) | 117.8 (10) | N(4)–C(16)–C(15) | 122 (1) |
| N(1)–C(1)–C(2) | 124 (1) | | |

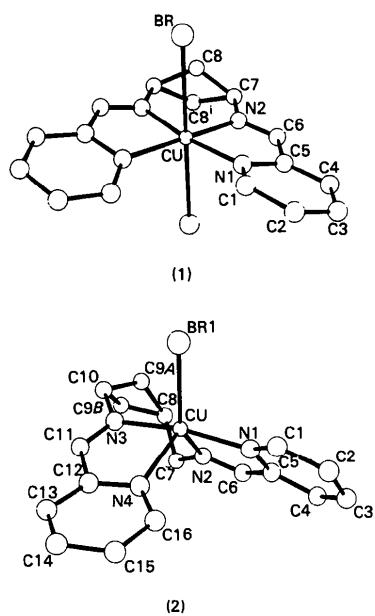


Fig. 1. PLUTO drawings of the two complexes and numbering schemes.

the atom at the apex of the pyramid [Br(1)] to positions such that the angles they make with the Cu and the bromine atom are about 120°. In this complex N(2)—Cu—Br(1) = 139.5 (3) and N(4)—Cu—Br(1) = 106.9 (3)°.

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Structure of a Hydrogen-Bonded Dinuclear Nickel 8-Quinolinol Complex

BY HIDEKO KIRIYAMA, YURIKO YAMAGATA, KYOKO YONETANI AND EIICHI SEKIDO

Department of Chemistry, Faculty of Science, Kobe University, Nada, Kobe 657, Japan

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Abstract. 8-Hydroxyquinolinium bis{tris- μ -[bis(8-quinolinolato)hydrogen(I)-N,O]-dinickel(II)} triperchlorate, [C₉H₈NO][Ni₂{H(C₉H₆NO)₂}₃]₂(ClO₄)₃, M_r = 2415.2, monoclinic, Cc , a = 45.313 (3), b = 13.143 (1), c = 18.675 (1) Å, β = 98.87 (1)°, V = 10989 (1) Å³, Z = 4, D_m = 1.48 (1), D_x = 1.46 Mg m⁻³, λ (Cu K α) = 1.5418 Å, μ = 2.102 mm⁻¹, $F(000)$ = 4968, T = 295 K, R = 0.0837 for 4668 observed reflections. Each Ni^{II} atom is octahedrally coordinated by three bidentate 8-quinolinol ligands in the facial conformation and two such complexes form a dinuclear cation through three strong O...H...O hydrogen bonds with distances ranging from 2.35 (2) to 2.55 (2) Å, as found in the triiodide analogue. The uncoordinated 8-quinolinol is linked by hydrogen bonds to two perchlorate ions, while the remaining perchlorate ion is disordered over two positions with nearly equal occupancies. Thus, the two anionic species, [(C₉H₈NO)(ClO₄)₂]⁻ and ClO₄⁻, are

held alternately between layers consisting of only cationic complexes [Ni₂{H(C₉H₆NO)₂}₃]⁺ parallel to (100).

Introduction. The previous X-ray study on the nickel 8-quinolinol complex with the triiodide anion (Kiriyama, Fukuda, Yamagata & Sekido, 1985) revealed that the complex cations of nickel with three bidentate 8-quinolinol ligands in facial conformation form a dinuclear cation of [Ni₂{H(C₉H₆NO)₂}₃]⁺ joined face to face by three strong O...H...O hydrogen bonds. Such unique dimer formation was noted as the first example for metal 8-quinolinol complexes. We prepared successively nickel 8-quinolinol complexes with perchlorate anions in order to ascertain whether or not such a dinuclear cation would be formed in the presence of another anion such as perchlorate. Its chemical composition was too complex to be confirmed