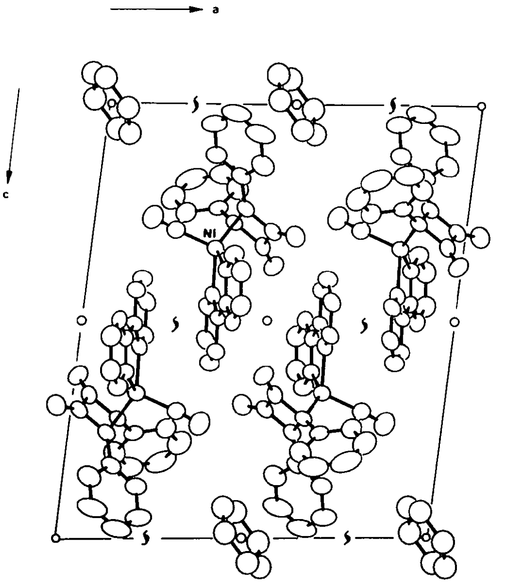

Fig. 2. The packing of the title compound in the unit cell, viewed down **b** looking towards the origin. The six C atoms defining the disordered toluene molecule are shown as circles with a radius of 0·3 Å.

The C12=C13 bond is 1·44 (1) Å and is shorter than that found in the Pt complex [1·53 (3) Å], but longer than that in phenylcyclobutenedione (Wong, Marsh & Schomaker, 1964), which itself has an olefinic bond length of 1·358 (6) Å. Bond lengths within the cyclobutenedione ring are otherwise comparable with those in the Pt compound. Bond distances and angles in the remainder of the molecule are as expected. The phenyl rings attached to C12 and C13 are bent out of the plane of the four-membered ring away from the Ni atom (C16–C21 23·2; C22–C27 19·2°) and are twisted by different amounts about the bonds linking them to the four-membered ring (Table 2). One, defined by the atoms C16–C21, is almost coplanar with a plane passing through Ni, C11 and C13 whereas the other lies almost coplanar (22°) with the four-membered ring. This asymmetry is also reflected in the bond lengths of the Ni atom to the C atoms of the cyclobutene ring and may be a result of crystal packing forces. There are, however, no intermolecular contacts between non-H atoms less than 3·2 Å. Fig. 2 shows the packing of the molecules in the unit cell.

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Structure of the Orange Modification of Diisobutylammonium Tetrachlorocuprate(II)

By M. Koman, V. Siroklin and G. Ondrejovič

Department of Inorganic Chemistry, Slovak Technical University, 812 37 *Bratislava, Czechoslovakia*

and A. B. Corradi and L. P. Battaglia

Istituto di Chimica Generale ed Inorganica, Università di Parma, Centro di Studio per la Strutturistica Diffrattometrica dell CNR, 431 00 *Parma, Italy*

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Abstract. $[NH_2(C_4H_9)_2]_2[CuCl_4]$, $M_r = 465·92$, tetragonal, $I\bar{4}$, $a = 16·731\,(5)$, $c = 9·095\,(4)$ Å, $V = 2545·9$ Å^3, $Z = 4$, $D_m = 1·217$, $D_x = 1·22$ g cm^{-3}, $\lambda(\text{Mo}\,K\alpha) = 0·71069$ Å, $\mu = 13·1$ cm^{-1}, $F(000) = 988$, $T = 293$ K, $R = 0·048$ for 919 reflections with $I > 3\sigma(I)$. The crystal structure of $[(^i\text{Bu})_2NH_2]_2[CuCl_4]$ consists of two symmetrically independent $CuCl_4^{2-}$ anions in special positions and $[(^i\text{Bu})_2NH_2]^+$ cations in

Table 1. *Atom coordinates and equivalent isotropic temperature factors* (Å^2) *with e.s.d.'s in parentheses*

	x	y	z	U_{eq}^*
Cu(1)	0·0	0·0	0·0	0·034 (1)
Cu(2)	0·0	0·5	0·25	0·043 (1)
Cl(1)	0·1212 (1)	0·0342 (1)	0·0879 (1)	0·062 (1)
Cl(2)	0·0781 (1)	0·5966 (1)	0·1579 (3)	0·070 (2)
N	0·2556 (4)	−0·0490 (4)	−0·1181 (9)	0·056 (4)
C(1)	0·2198 (5)	−0·0626 (6)	−0·2696 (12)	0·061 (6)
C(2)	0·2243 (6)	0·0101 (6)	−0·3632 (12)	0·067 (6)
C(3)	0·1877 (11)	−0·0076 (11)	−0·5123 (19)	0·128 (11)
C(4)	0·1835 (8)	0·0841 (8)	−0·2959 (14)	0·098 (9)
C(5)	0·2692 (6)	−0·1266 (6)	−0·0378 (12)	0·057 (6)
C(6)	0·2925 (9)	−0·1148 (9)	0·1200 (15)	0·100 (9)
C(7)	0·3006 (10)	−0·1975 (9)	0·1901 (20)	0·143 (13)
C(8)	0·3585 (12)	−0·0640 (13)	0·1490 (19)	0·158 (13)

* Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 2. *Interatomic distances* (Å) *and bond angles* (°) *with e.s.d.'s in parentheses*

Cu(1)—Cl(1)	2·255 (2)	Cl(1)—Cu(1)—Cl(1)*	138·6 (1)
Cu(2)—Cl(2)	2·242 (2)	Cl(1)—Cu(1)—Cl(1)	97·18 (6)
N—C(1)	1·516 (5)	Cl(2)—Cu(2)—Cl(2)*	136·3 (1)
C(1)—C(2)	1·486 (5)	Cl(2)—Cu(2)—Cl(2)	97·98 (6)
C(2)—C(3)	1·523 (7)	C(1)—N—C(5)	111·62 (3)
C(2)—C(4)	1·542 (6)	N—C(1)—C(2)	112·0 (3)
N—C(5)	1·507 (4)	C(1)—C(2)—C(3)	109·3 (3)
C(5)—C(6)	1·496 (7)	C(1)—C(2)—C(4)	114·2 (3)
C(6)—C(7)	1·530 (6)	C(3)—C(2)—C(4)	109·4 (4)
C(6)—C(8)	1·419 (8)	N—C(5)—C(6)	112·8 (3)
N···Cl(1)	3·240 (8)	C(5)—C(6)—C(7)	107·5 (5)
N···Cl(2)	3·285 (7)	C(5)—C(6)—C(8)	117·4 (5)
		C(7)—C(6)—C(8)	113·3 (5)

* 'Flattening' angles (Smith, 1976).

general positions. The two Cu^{II} atoms are tetrahedrally coordinated by four Cl atoms with Cu(1)—Cl(1) distances 2·255 (1) and Cu(2)—Cl(2) 2·242 (1) Å. The Cl(1)—Cu(1)—Cl(1) and Cl(2)—Cu(2)—Cl(2) 'flattening' angles are 138·6 (1) and 136·3 (1)°. The $[(^iBu)_2NH_2]^+$ cations and $CuCl_4^{2-}$ anions are linked by N—H···Cl hydrogen bonds.

Introduction. The stoichiometry and stereochemistry of solid chlorocuprate(II) salts with isobutylammonium cations were recently studied (Biela & Siroklin, 1988). Three modifications of $[(^iBu)_2NH_2]_2[CuCl_4]$ were prepared: yellow, red and orange. On the basis of electronic spectra the $CuCl_4^{2-}$ anions in all three modifications are shown to possess a distorted tetrahedral structure. The structure of the orange modification is, however, significantly different from those of the yellow and red modifications.

Experimental. Orange tetragonal bipyramidal crystal, 0·30 × 0·30 × 0·60 mm, D_m by flotation, Philips PW 1100 diffractometer, 25 reflections for lattice-parameter determination, $23 < 2\theta < 31°$, absorption correction (min.–max.) 1·00–1·17, $2\theta_{max} = 50°$, *hkl* range 0, 0, 0 to 19, 19, 10, two standard reflections every 98 reflections, 1285 reflections measured with $3 \leq \theta \leq 25°$, 919 with $I > 3\sigma(I)$. Cu^{II}- and Cl-atom positions from Patterson map; other non-H atoms from Fourier map. H atoms from difference Fourier map (*SHELX*76, Sheldrick, 1976). Anisotropic full-matrix refinement (except H atoms) based on F, $w = k/[\sigma^2(F_o) + gF_o^2]$, with $k = 0{\cdot}9672$, $g = 0{\cdot}0035$, $wR = 0{\cdot}0527$, $R = 0{\cdot}0484$; $(\Delta/\sigma)_{max}$ in final least-squares cycle 0·37. Min. and max. height in final $\Delta\rho$ synthesis −0·37 and 0·32 e Å^{-3}. Atomic scattering factors were those incorporated in *SHELX*76.

Discussion. Final atomic parameters for non-H atoms are listed in Table 1, interatomic distances and bond angles in Table 2.* The packing of the ions in the unit cell is shown in Fig. 1. Two symmetrically independent $CuCl_4^{2-}$ anions are found in the structure, with interatomic distances and angles similar to those observed in other chlorocuprates (Smith, 1976). The Cu—Cl distances in $CuCl_4^{2-}$ anions range from 2·209 (4) (Harlow, Wells, Watt & Simonsen, 1974) to 2·271 (10) Å (Anderson & Willett, 1971). The 'flattening' angles [defined by Smith (1976)] in tetra-

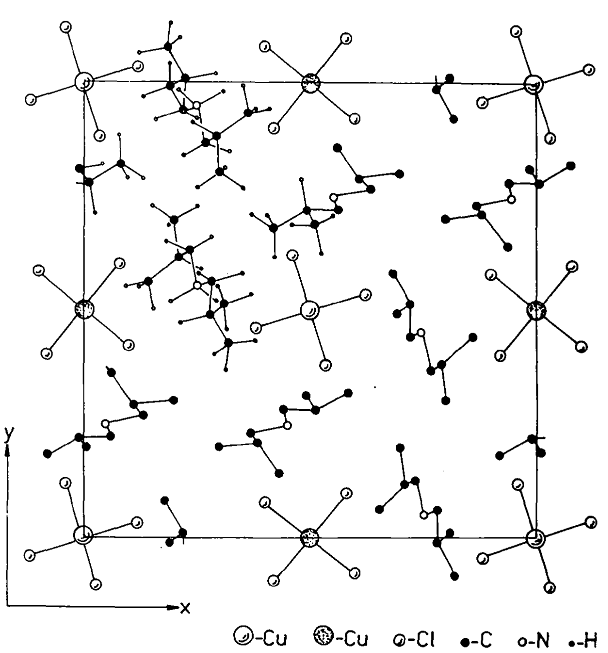

Fig. 1. Packing of the molecules projected along **c** with H atoms in one quarter of the unit cell.

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* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44665 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

chlorocuprate(II) salts range from 110·6 (4) (Clay, Murray-Rust & Murray-Rust, 1973) to 159 (3)° (Anderson & Willett, 1971).

The diisobutylammonium cation is linked to Cl atoms of $CuCl_4^{2-}$ anions by hydrogen bonds: $Cl(1)\cdots H(1) = 2{\cdot}144$ (2) and $Cl(2)\cdots H(2) = 2{\cdot}248$ (2) Å. The $N-H(1)\cdots Cl(1)$ angle is 173·2 (4)° and the $N-H(2)\cdots Cl(2)$ angle is 165·8 (4)°, with $N\cdots Cl(1) = 3{\cdot}240$ (8) and $N\cdots Cl(2) = 3{\cdot}285$ (7) Å. The $N\cdots Cl$ interatomic distances for tetrachlorocuprates span the range 3·11 (Lamotte-Brasseur, Dupont & Dideberg, 1973) to 3·55 Å (Russell & Wallwork, 1969).

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Structure of Tetrakis(biuret)samarium(III) Perchlorate

By Salim F. Haddad

Department of Chemistry, The University of Jordan, Amman, Jordan

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Abstract. $[Sm(C_2H_5N_3O_2)_4](ClO_4)_3$, $M_r = 861{\cdot}02$, monoclinic, $P2_1/c$, $a = 11{\cdot}90$ (2), $b = 12{\cdot}41$ (2), $c = 19{\cdot}93$ (4) Å, $\beta = 92{\cdot}5$ (1)°, $V = 2940$ (16) Å^3, $Z = 4$, $D_m = 2{\cdot}010$, $D_x = 1{\cdot}945$ g cm^{-3}, λ(Cu $K\alpha$) = 1·5418 Å, $\mu = 172$ cm^{-1}, $F(000) = 1700$, ambient temperature, $R = 0{\cdot}107$ for 1313 reflections with $\sin^2\theta > 0{\cdot}1$. All atoms in general positions. The four neutral biuret ligands chelate *via* carbonyl O atoms to Sm^{III} in a rather planar *trans–trans* configuration with a mean twist of 9·4 (2·7)° about the oxygen–oxygen line. The six-membered rings formed with Sm are folded by a mean value of 11·4 (6·3)° about the oxygen–oxygen line. The mean chelate bite angle is 69·9 (1·0)°. The four bidentate ligands span opposite edges of the two rectangular faces of an approximate square antiprism (D_{4d}). The three perchlorate moieties are ionic but deviate significantly from tetrahedral geometry, possibly due to hydrogen bonding, and exhibit rather high thermal parameters.

Introduction. Series of alkaline-earth and lanthanide halides, nitrates and perchlorate complexes with biuret were prepared by us and the crystal structures of tetrakis(biuret)strontium(II) perchlorate (Haddad & Gentile, 1975) and tetrakis(biuret)samarium(III) nitrate (Haddad, 1987) reported. The structure determination of tetrakis(biuret)samarium(III) perchlorate was undertaken as a prototype of lanthanide(III) perchlorate complexes with biuret. As indicated by preliminary X-ray photographs of the *h*0*l* zones all lanthanide(III) perchlorate complexes with biuret prepared under the same conditions are isostructural with tetrakis(biuret)samarium(III) perchlorate and belong to space group $P2_1/c$.

To our knowledge other X-ray structures of biuret and its complexes reported are those of biuret hydrate (Hughes, Yakel & Freeman, 1961), bis(biuret)cadmium(II) chloride (Cavalca, Nardelli & Fava, 1960), bis(biuret)copper(II) chloride (Freeman, Smith & Taylor, 1961), and bis(biuret)zinc(II) chloride (Nardelli, Fava & Giraldi, 1963). All of the above complexes of biuret are with transition metals.

Experimental. Biuret, $NH_2CONHCONH_2$, and hydrated samarium(III) perchlorate in the molar ratio of 6:1 were refluxed in minimum 95% ethanol for two days. An equal volume of *n*-butanol was then added and the mixture allowed to evaporate slowly in warm (320 K) dry atmosphere. Clear white crystals suitable for X-ray diffraction work separated as a second crop after several days. Dried *in vacuo*. M.p. 490 K (dec.). Analysis calculated for $Sm(C_2H_5N_3O_2)_4(ClO_4)_3$: C 11·16, N 19·52, H 2·34, Sm 17·46%; found: C 11·26, N 19·55, H 2·40, Sm 17·37%.

Density measured by flotation in carbon tetrachloride and methylene iodide. Unit-cell translations were determined from rotation photographs about *a*, *b* and *c* by extrapolation to a Bragg angle of 90° with σ of the intercept reported. β was determined from a Weissenberg photograph of the *h*0*l* zone with σ of the

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