[18] *S. J. Cristol, R. M. Sequeira & C. H. DePuy*, J. Amer. chem. Soc. *87*, 4007 (1965).
[19] *S. R. Sandler*, J. org. Chemistry *32*, 3876 (1967).
[20] *P. Weyerstahl, R. Mathias & G. Blume*, Tetrahedron Letters *1973*, 611.
[21] *M. Schlosser & G. Heinz*, Angew. Chem. *79*, 617 (1967); Angew. Chem. internat. Ed. *6*, 629 (1967).
[22] *M. Makosza*, Tetrahedron Letters *1969*, 673, 677.
[23] *M. Schlosser, B. Spahić, C. Tarchini & Le Van Chau*, Angew. Chem. *87*, 346 (1975); Angew. Chem. internat. Edit. *14*, 365 (1975).
[24] *D. Seyferth*, Accounts Chem. Res. *5*, 65 (1972).
[25] *D. Seyferth & G. J. Murphy*, J. organometal. Chemistry *49*, 117 (1973).
[26] *H. Eggerer & F. Lynen*, Liebigs Ann. Chem. *630*, 58 (1960).
[27] *S. M. McElvain & M. J. Curry*, J. Amer. chem. Soc. *70*, 3781 (1948).
[28] *R. A. Moss & R. Gerstl*, Tetrahedron *23*, 2549 (1967), insbesondere S. 2552.

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284. Proof of the Existence of a Linear, Centrosymmetric Polyiodide Ion I_4^{2-}: The Crystal Structure of $Cu(NH_3)_4 I_4$

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(23. X. 75)

Summary. Tetrammine-copper(II)-tetraiodide $Cu(NH_3)_4I_4$ crystallizes in the monoclinic space group C 2/m. The crystal structure has been determined from X-ray diffractometer data and refined to $R_w = 2.2\%$. Four coplanar nitrogen atoms and two axial iodine atoms form an octahedral coordination around Cu(II) with a pronounced 4 + 2 tetragonal distortion. A connection of the Cu(II) atoms by linear, centrosymmetric I_4^{2-} polyiodide ions results in infinite chains of $[Cu(NH_3)_4^{2+} I_4^{2-}]$-units. The central I-I-bond distance in I_4^{2-} is 2.802(1) Å; a considerable amount of I-I bonding is indicated by the distance of 3.342(1) Å found for the terminal bonds. These intramolecular bond distances correspond to calculated I-I-bond orders of 0.80 and 0.43.

Introduction. – Although Cu(II)ions are normally reduced by I^- ions in solution, several cupric iodide complexes can be isolated as solids. Concerning the crystal structures of nonchelated copper(II)iodide complexes, few data are available at present. In $Cu_2(OH)_3I$ [1] and in $Cu^{II}(NH_3)_4(Cu^{I}I_2)_2$ [2], the I^- ions occupy the axial positions of a 4 + 2 elongated distorted octahedral coordination around Cu. The formation of a 4 + 2 distorted octahedral coordination polyhedra in Cu(II) complexes may be described as a consequence of the *Jahn-Teller* theorem [3] and has also been observed in compounds containing isolated $[CuL_6]^{n\pm}$ units with six identical ligands L as *e.g.* in $Ba_2Cu(OH)_6$ [4].

Recently, single crystals of tetrammine-copper(II)-tetraiodide, $Cu(NH_3)_4I_4$, a complex first described by *Jörgensen* [5], have been prepared and investigated by *Weissenberg*, precession and powder X-ray methods [6]. Accurate cell dimensions were determined by a least-squares fit of the orientation angles of 12 reflections measured on a four-circle diffractometer: a = 14.172(4) Å, b = 8.926(2) Å, c = 6.558(2) Å, β = 128.65(2)°, space group C 2/m, 2 formula units per cell. In order to elucidate the coordination behaviour in a copper(II)iodide compound and to determine the configuration of the polyiodide group ($I_2 + 2I^-$, $I_3^- + I^-$ or I_4^{2-} ?), we have solved the crystal structure of $Cu(NH_3)_4I_4$.

Experimental Part. – A single crystal with approximate dimensions 0.15 × 0.15 × 0.20 mm³ was chosen for data collection on a computer-controlled *Picker* FACS-I diffractometer, using MoK_α radiation monochromatized by reflection from a pyrolytic graphite plate. Intensity data were measured by a θ–2θ scan over a 2 θ-range of 2° (plus the α_1–α_2 dispersion) with a scan speed of 0.5°/min. Background counts of 40 sec. were taken at each side of the peak. Three standard reflections chosen to lie in different regions of reciprocal space were monitored at regular intervals and used for an internal scaling of the data by least-squares methods. The net counts of the standard reflections did not alter appreciably over the period of data collection, indicating that the capillary mounting prevented crystal decomposition. Intensities were collected up to $2\theta \leqslant 60°$. Of the 1704 reflections measured (including standards), 1008 remained after averaging equivalent reflections and 830 were judged to be observed according to the criterion $I \geqslant 2\sigma(I)$, $\sigma(I)$ being the estimated standard deviation of the net intensity based on counting statistics. The intensities were reduced to F_o in the usual way, applying a correction for absorption ($\mu = 108.3\ \mathrm{cm}^{-1}$ for MoK_α radiation). All computations, including subsequent refinement of the structure, were performed using the program system XRAY [7] on a CDC 6400/6500 computer at the ETH Zurich. The atomic scattering factors were computed according to *Cromer et al.* [8]. Corrections for anomalous dispersion and secondary extinction were included in the refinement cycles. A table of observed and calculated structure factors is available from the authors on request.

Structure Analysis and Refinement. – Approximate positions of the heavy atoms could be deduced from a three-dimensional *Patterson* synthesis. The two Cu atoms are in the special position 2(b), the eight I atoms in two sets of fourfold special positions 4(i). Structure-factor calculations based on refined positions of these heavy atoms with isotropic temperature factors yielded a conventional R-value ($= \Sigma||F_o| - |F_c||/\Sigma|F_o|$) of 0.18. At this stage a difference map showed peaks corresponding to all the N atoms. Introduction of anisotropic temperature factors and subsequent cycles of full-matrix least-squares refinement decreased R to 0.032 and the weighted R_w ($= [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$) to 0.029. The function minimized was $\Sigma w(|F_o| - |F_c|)^2$, where w is the weight derived from counting statistics and defined as $w = 1/\sigma^2_{F_o}$. Since a final difference map failed to show meaningful positions for the H atoms, approximate H positions were calculated from stereochemical assumptions and held invariant in the least-squares refinement, leading to R = 0.031 and R_w = 0.022 for all observed reflections.

Results and Discussion of the Structure. – Positional coordinates and vibrational parameters are listed in Tables 1 and 2.

Table 1. *Positional and thermal parameters.* Standard deviations in the last digit calculated in the final least-squares refinement are given in brackets

	x	y	z	U(Å² × 10²) [a]
Cu	0	0.5	0	3.79(15)
I(1)	0.0872(1)	0	0.4628(1)	5.53(10)
I(2)	0.2951(1)	0	0.3739(1)	4.83(9)
N	0.4072(4)	0.1594(5)	0.0251(7)	4.81(53)
H(1)	0.393	0.124	0.149	6.33
H(2)	0.329	0.177	0.849	6.33
H(3)	0.456	0.253	0.093	6.33

[a] Isotropic thermal parameters are those before anisotropic refinement.

Table 2. *Mean-square amplitudes of vibration* (Å² × 10⁴). The temperature factors were calculated from the expression: $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cu	460(7)	320(7)	540(7)	0	311(6)	0
I(1)	473(4)	423(3)	561(3)	0	125(3)	0
I(2)	463(3)	545(4)	418(3)	0	238(2)	0
N	507(27)	364(25)	550(24)	−3(21)	314(22)	−12(19)

The resulting interatomic distances and bond angles are summarized in Table 3.

Table 3. *Interatomic distances* (Å) *and bond angles* (°) *in* $Cu(NH_3)_4I_4$ *with their estimated standard deviations.* Symmetry code:

i	x	y	z	vii	x − 1/2	1/2 − y	z
ii	x − 1/2	y + 1/2	z	viii	1/2 − x	1/2 + y	− z
iii	x − 1/2	y + 1/2	z − 1	ix	x	y	1 + z
iv	− x	y	1 − z	x	1 − x	− y	1 − z
v	1/2 − x	1/2 − y	1 − z	xi	− x	y	− z
vi	1/2 − x	1/2 − y	− z	xii	1/2 − x	y − 1/2	1 − z

a) *$Cu(NH_3)_4I_2$-octahedron*

$\mathrm{Cu^{i} - N^{ii,\,vi,\,vii,\,viii}}$	$\mathrm{Cu^{i} - I(2^{iii,\,v})}$	N—Cu—N	N—Cu—N
2.013(5) (4×)	3.224(1) (2×)	89.96(20) (2×)	90.04(20) (2×)
N—Cu—I(2)	N—Cu—I(2)	N—Cu—N	$\mathrm{I(2^{iii})\text{-}Cu\text{-}I(2^{v})}$
89.39(9) (4×)	90.61(9) (4×)	180.0 (2×)	180.0 (1×)

b) *I_4^{2-}-polyiodide ion*

$\mathrm{I(1^{i}) - I(1^{iv})}$	I(1) – I(2)	I(2) – I(1) – I(1)
2.802(1)	3.342(1) (2×)	180.00(1) (2×)

c) *Shortest nonbonding distances of copper and iodine*

$\mathrm{Cu^{i} - I(1^{iii,\,v})}$	$\mathrm{Cu^{i} - I(2^{ii,\,vi})}$	$\mathrm{I(1^{i}) - I(2^{v,\,xii})}$	$\mathrm{I(1^{i}) - I(2^{xi})}$
4.571(1) (2×)	4.830(1) (2×)	4.649(1) (2×)	4.727(1)
$\mathrm{I(1^{i}) - I(2^{ix})}$	$\mathrm{I(1^{i}) - I(1^{xi})}$	$\mathrm{I(2^{i}) - I(2^{x})}$	
4.731(1)	4.924(1)	4.943(1)	

Four coplanar N atoms and two I atoms form an octahedral coordination around Cu(II) with a pronounced 4 + 2 tetragonal distortion. The equatorial Cu–N– bond length of 2.013(5) Å agrees with corresponding values in similar elongated tetragonal complexes [9], whereas the Cu–I distance of 3.224(1) Å is about 0.35 Å larger than the sum of the ionic radii of Cu^{2+} and I^-. This may favour the chemical stability of the compound by preventing the redox reaction $Cu^{2+} + I^- \rightarrow Cu^+ + {}^1/_2\, I_2$. Corresponding Cu–I distances are 3.08(1) Å and 3.13(1) Å in $Cu_2(OH)_3I$ [1] and 3.17(1) Å in $Cu(NH_3)_4(CuI_2)_2$ [2]. Fig. 1 shows the $Cu(NH_3)_4I_2$-unit.

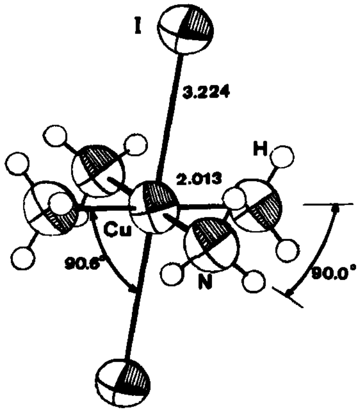

Fig. 1. *Coordination geometry of the Cu(II)polyhedron in $Cu(NH_3)_4I_4$.* The thermal ellipsoids in Fig. 1, 2 and 3 correspond to a probability of 74%

Connection of the Cu(II)atoms by linear I_4^{2-} polyiodide ions results in infinite chains of $[Cu(NH_3)_4^{2+}I_4^{2-}]$ (Fig. 2), which are packed together in a three-dimensional arrangement as shown in Fig. 3.

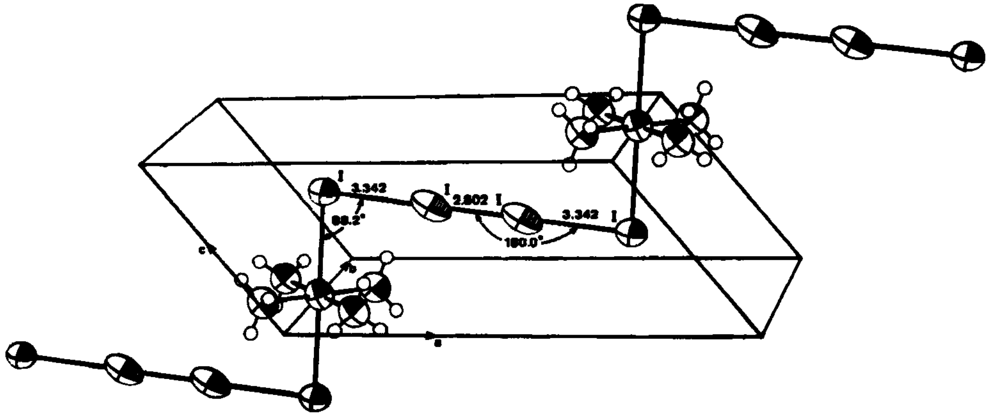

Fig. 2. *A perspective drawing of the polyiodide ion* I_4^{2-} *within infinite chains of* $[Cu(NH_3)_4^{2+}I_4^{2-}]$*-units and corresponding interatomic distances and bond angles*

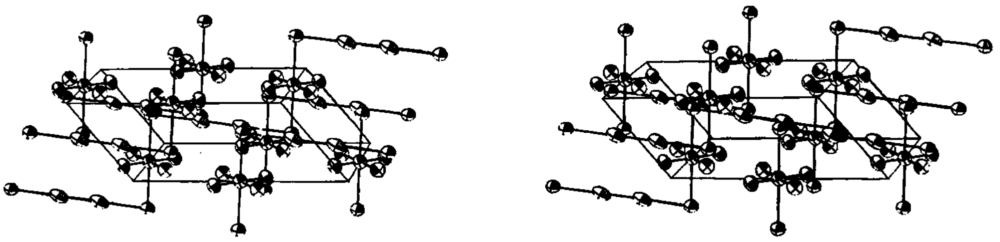

Fig. 3. *Stereoscopic view of the packing of infinite* $[Cu(NH_3)_4^{2+}I_4^{2-}]$*-chains in the unit cell*

Apart from a short communication on nonstoichiometric complex uranyl halides [10], $Cu(NH_3)_4I_4$ represents the first well established example of a compound with discrete I_4^{2-} ions in the solid state. However, studies of NMR. line broadening in aqueous solutions containing I^- and I_3^- have been interpreted [11] in terms of formation of I_4^{2-} as intermediate in the exchange process. The centrosymmetric I_4^{2-} units in $Cu(NH_3)_4I_4$ are perfectly colinear. The central I–I distance of 2.802(1) Å is significantly larger than the value of 2.715 Å recently determined in a low-temperature study of crystalline I_2 [12]. Since the I–I *van der Waals* distance is about 4.30 Å, considerable I–I bonding is indicated by the distance of 3.342(1) Å found for the terminal bonds in I_4^{2-}. In all polyiodides studied so far, more or less discrete ions can be picked out with one or two short distances of about 2.7–2.9 Å alternating with distances of about 3.1–3.5 Å. This would suggest I_2 molecules interacting with I^- or I_3^- ions. Following this interpretation, I_4^{2-} would correspond to interaction of two I^- ions with one I_2 molecule, *i.e.* $I^{\delta-}(I\text{–}I)I^{\delta-}$. In contrast to many higher polyiodides, however, – *e.g.* I_5^- in $N(CH_3)_4I_5$, I_9^- in $N(CH_3)_4I_9$ and I_{16}^{4-} in (Theobromine)$_2$ · H_2I_8 (see Table 4) – I_4^{2-} is a well defined discrete polyiodide group since the shortest distance of 4.649(1) Å between neighbouring I_4^{2-} units is larger than the *van der Waals* distance. Table 4 lists intra- and intermolecular distances in I_2 and in various polyiodides.

Table 4. *Intramolecular and intermolecular distances in iodine and polyiodides.* I – I signifies distances within iodine molecules or within the indicated polyiodide ions, whereas I · · · I represents the shortest distances between neighbouring units

Compound	Polyiodide ion	I – I (Å)	I · · · I (Å)	Ref.
I_2 gas	–	2.662	–	1955, [13]
I_2 solid, 20°C	–	2.68	3.56	1953, [14]
I_2 solid, –163°C	–	2.715	3.50	1967, [12]
CsI_3	I_3^-	2.84, 3.04	4.01	1972, [15]
$(C_6H_5)_4AsI_3$	I_3^-	2.92, 2.92	>4.30	1972, [15]
$Cu(NH_3)_4I_4$	I_4^{2-}	2.80, 3.34 (2×)	4.65	This work
$N(CH_3)_4I_5$	I_5^-	2.81 (2×), 3.17 (2×)	3.63	1957, [16]
Cs_2I_8	I_8^{2-}	2.83, 2.84 (2×), 3.00 (2×), 3.42 (2×)	3.90	1954, [17]
$N(CH_3)_4I_9$	I_9^-	2.67 (2×), 2.90, 2,91, 3.18, 3.24 (2×), 3.43	3.49	1955, [18]
(Theobromine)$_2$ · H_2I_8	I_{16}^{4-}	2.76 (2×), 2.84 (2×), 2.92 (2×), 2.94 (2×), 3.03 (2×), 3.35 (2×), 3.42 (2×), 3.45	3.84	1975, [19]

An analogous linear group Br_4^{2-} with Br–Br distances of 2.43 Å and 2.98 Å (2×) occurs in W_6Br_{16} [20]. Although these values suffer from large standard deviations (± 0.04 Å), an attempt has been made to correlate the bond lengths in I_4^{2-} and Br_4^{2-} in terms of 'calculated bond orders' given for various polyhalogens by *Wiebenga &*

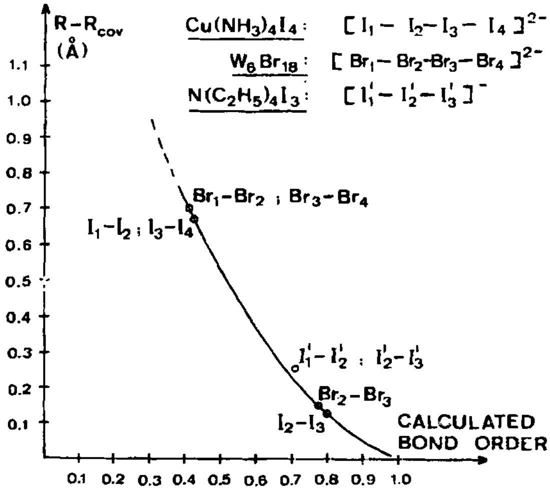

Fig. 4. *Experimental bond lengths* vs. *calculated bond orders* [21] *for I_4^{2-} and Br_4^{2-}*. I_3^- is included for comparison. R is the experimental bond length and R$_{cov}$ the sum of the covalent radii.

Kracht [21]. By means of a modified *Hückel* theory, using p functions of the valence shell only, these authors derived a correlation between R–R_{cov} and calculated bond orders (see Fig. 4). The resulting bond orders for I_4^{2-} and Br_4^{2-} are very similar: 0.80 (I_4^{2-}) and 0.78 (Br_4^{2-}) for the central bond, 0.43 (I_4^{2-}) and 0.41 (Br_4^{2-}) for the terminal bonds.

It would be interesting also to study the bonding character of I_4^{2-} using a 4 centre-6 electron MO model, as carried out for Br_4^{2-} by *Müller* [22].

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REFERENCES

[1] *H. R. Oswald, Y. Iitaka, S. Locchi & A. Ludi*, Helv. *44*, 2103 (1961).
[2] *J. A. Baglio, H. A. Weakliem, F. Demelio & P. A. Vaughan*, J. inorg. nucl. Chemistry *32*, 795 (1970).
[3] *H. A. Jahn & E. Teller*, Proc. Roy. Soc. A *161*, 220 (1937).
[4] *E. Dubler, P. Korber & H. R. Oswald*, Acta crystallogr. B *29*, 1929 (1973).
[5] *S. M. Jörgensen*, Ber. deutsch. chem. Ges. *2*, 460 (1869).
[6] *H. R. Oswald & M. Textor*, to be published.
[7] *J. M. Stewart, F. A. Kundell & J. C. Baldwin*, XRAY SYSTEM, Computer Science Center, Univ. of Maryland 1970.
[8] *D. Cromer & J. Mann*, Acta crystallogr. A *24*, 321 (1968).
[9] *B. J. Hathaway & P. G. Hodgson*, J. inorg. nucl. Chemistry *35*, 4071 (1973).
[10] *Y. N. Mikhailov, V. G. Kuznetsov & E. S. Kovaleva*, Ž. Strukt. Chim. *9*, 710 (1968).
[11] *E. E. Genser & R. E. Connick*, J. chem. Physics *58*, 990 (1973).
[12] *F. van Bolhuis, P. B. Koster & T. Migchelsen*, Acta crystallogr. *23*, 90 (1967).
[13] *I. L. Karle*, J. chem. Physics *23*, 1739 (1955).
[14] *A. I. Kitaigorodskii, T. L. Khotsyanova & Y. T. Struchkov*, Ž. Fiz. Chim. *27*, 780 (1953).
[15] *J. Runsink, S. Swen-Walstra & T. Migchelsen*, Acta crystallogr. B *28*, 1331 (1972).
[16] *J. Broekema, E. E. Havinga & E. H. Wiebenga*, Acta crystallogr. *10*, 596 (1957).
[17] *E. E. Havinga, K. H. Boswijk & E. H. Wiebenga*, Acta crystallogr. *7*, 487 (1954).
[18] *W. J. James, R. J. Hach, D. French & R. E. Rundle*, Acta crystallogr. *8*, 814 (1955).
[19] *F. H. Herbstein & M. Kapon*, J. chem. Soc. Chem. Commun. *1975*, 677.
[20] *R. Siepmann & H. G. von Schnering*, Z. anorg. allg. Chem. *357*, 289 (1968).
[21] *E. H. Wiebenga & D. Kracht*, Inorg. Chemistry *8*, 738 (1969).
[22] *H. Müller*, Theoret. chim. Acta *21*, 110 (1971).