Pergamon

Polyhedron Vol. 14, No. 5, pp. 649–654, 1995
Copyright © 1995 Elsevier Science Ltd
Printed in Great Britain. All rights reserved
0277–5387/95 $9.50+0.00

0277-5387(94)00289-4

SYNTHESIS AND CRYSTAL STRUCTURE OF BIS[(7,9-DIAZA-3,14-DITHIATETRACYCLE[15,4,0,0^{4,5},0^{13,14}]NONACOSA-1(17),18,20,4(22),23,25,13(26),27,29-NONAENE)CHLOROCOPPER(II)] TETRACHLORODICUPRATE(I) BISMETHANOL. ATYPICAL NON-PLANAR CONFORMATION OF THE $[Cu_2Cl_4]^{2-}$ ANION

LLUIS ESCRICHE, NATIVIDAD LUCENA and JAUME CASABÓ*

Department de Química, Universitat Autònoma de Barcelona, 08193 Bellaterra,
Barcelona, Spain

and

FRANCESC TEIXIDOR*

Institut de Ciència dels Materials (C.S.I.C.), Campus de Bellaterra, 08193 Bellaterra,
Barcelona, Spain

and

RAIKKO KIVEKÄS

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

and

REIJO SILLANPÄÄ

Department of Chemistry, University of Turku, SF-20500 Turku, Finland

(*Received* 29 *March* 1994; *accepted* 15 *July* 1994)

Abstract—A doubly complex salt containing the atypical non-planar Cu^I dimeric anion $[Cu_2Cl_4]^{2-}$ and a Cu^{II} containing macrocyclic cation has been synthesized starting from $CuCl_2 \cdot 2H_2O$ and a new N_2S_2 type macrocycle 7,9-diaza-3,14-dithiatetracycle [15,4,0,0^{4,5},0^{13,14}]nonacosa-1(17),18,20,4(22),23,25,13(26),27,29-nonaene. The structure of the complex was determined by X-ray crystallography.

Tetrahalodicuprates(I), $[Cu_2X_4]^{2-}$ (X = Cl, Br and I), have been obtained by two synthetic pathways. In the first one, the synthesis starts with stable Cu^I salts. For instance, $[Cu_2Br_4]^{2-}$ and $[Cu_2I_4]^{2-}$ were prepared from the fairly stable solids, CuBr or CuI, and the suitable quaternary ammonium or arsonium salts.[1] There are only two examples of the second synthetic method which involve reduction of Cu^{II} salts. The resulting $Cu_2Cl_4^{2-}$ complexes all include bulky metal-containing cations, e.g. the reduction of the Schiff base–Cu^{II} complex, Cu (salen)Cl_2, by V^{IV} salts has been reported to give the mixed Cu^I–V^V complex,[2] [VO(salen) (H_2O)] [Cu_2Cl_4].

Moreover, the planar $[Cu_2Cl_4]^{2-}$ anion was obtained either from the first method or the second method from reaction of CuCl or $CuCl_2$ and dmtp[3]

---

*Authors to whom correspondence should be addressed.

(dmtp = 5,7 - dimethyl [1, 2, 4] triazolo [1, 5 - α] pyrimidine) in hot ethanolic solutions yielding the all Cu^I compound, $[Cu_4(dmtp)_4Cl_2][Cu_2Cl_4]$.

In this report we describe the first mixed Cu^{II}–Cu^I compound containing the $[Cu_2Cl_4]^{2-}$ anion in a non-planar configuration and a new macrocyclic Cu(II) complex, $[Cu(C_{25}H_{28}N_2S_2)Cl]_2[Cu_2Cl_4]\cdot 2CH_3OH$.

EXPERIMENTAL

All operations were performed under dinitrogen. Solvents were dried and degassed by standard reported methods prior to use. Microanalyses were determined in our analytical laboratory using a Perkin–Elmer 240-B. ^1H-NMR spectra were obtained by using a Bruker AM 400 WB instrument. IR spectra were obtained as KBr pellets using a Perkin–Elmer 240FT spectrophotometer.

Synthesis of o-(2-*carboxiphenylthiomethyl*)*benzene* (**1**)

To a solution of thiosalicylic acid (Aldrich) (3 g, 18.8 mmol) in ethanol (100 cm^3), solid KOH (2.11 g, 37.7 mmol) and a solution of α,α′-dichloro-*o*-xylene (Aldrich) (1.65 g, 9.42 mmol) in ethanol (40 cm^3) were added under nitrogen. The mixture was poured out in water and acidified with HCl. The white solid precipitated was filtered, water washed and dried at 100°C. Yield 3.2 g (87%). IR (KBr): ν(C═O), 1678 cm^{-1}. ^1H NMR (ppm, DMSO-d^6): 4.33 (s, 4H, S—CH_2—Ar), 7.20–7.90 (m, 12H, Ar), 13 (s, 2, COOH). Found: C, 64.1; H, 4.3; S, 15.1. Calc. for $C_{22}H_{18}O_4S_2$: C, 64.4; H, 4.4; S, 15.6.

Synthesis of the amide-macrocycle (**2**)

o-(2-Carboxiphenylthiomethyl)benzene (**1**) (3 g, 7.3 mmol) was refluxed with $SOCl_2$ for 4 h to obtain the acid chloride derivative. To a solution of *o*-(2-chlorocarboxiphenylthiomethyl)benzene (3 g, 6.7 mmol) in dry toluene (600 cm^3), a solution of 1,3-diaminepropane (Aldrich) (1 g, 13.4 mmol) in dry toluene (50 cm^3) was added dropwise in high dilution conditions (2–3 $cm^3\ h^{-1}$). The mixture was refluxed for 1 h and filtered. The clear solution was evaporated and the white solid precipitated filtered off and recrystallized in 1,2-dimethoxyethane. Yield 1.3 g (42.5%). IR (KBr): ν(C═O), 1630 cm^{-1}. ^1H NMR (ppm, DMSO-d^6): 1.77 (m, 2H, N—CH_2—$\underline{CH_2}$—CH_2—N), 3.34 (t, 4H, N—$\underline{CH_2}$—CH_2—$\underline{CH_2}$—N), 4.26 (s, 4H, S—CH_2—Ar), 7.20–8.29 (m, 14H, Ar and N—H). Found: C, 67.1; N, 6.0; H, 5.6; S, 14.2. Calc. for $C_{25}H_{24}N_2S_2O_2$: C, 66.9; N, 6.2; H, 5.4; S, 14.2%.

Synthesis of 7,9-*diaza*-3,14-*dithiatetracycle*[15,4,0,$0^{4,5}$,$0^{13,14}$] *nonacosa*-1(17),18,20,4(22),23,25,13(26),27,29-*nonaene and the copper complex* (**3**)

To a solution of the amide macrocycle (**2**) (1 g, 2.23 mmol) in THF (1300 cm^3), $BH_3\cdot THF$ (100 cm^3, 1 M) was added. The mixture was refluxed for 4 days and allowed to stand at room temperature. The $BH_3\cdot THF$ in excess was eliminated by slow addition of cold water (25 cm^3). The solution was evaporated until a white solid appeared. The resulting solid was treated with a solution of HCl (100 cm^3, 2 M) and let to reflux for 4 h. The mixture was evaporated once again obtaining a white solid precipitate which was treated with 2 M KOH solution (100 cm^3) and extracted twice with CH_2Cl_2 (50 cm^3). The organic phase was dried with Na_2SO_4 and rotavaporated until a white solid appeared, which was treated with methanol (10 cm^3). The methanolic solution which contains the amine macrocycle was treated with a $CuCl_2\cdot 2H_2O$ methanolic solution (0.5 M, 13.4 cm^3). The pale-green colour of the solution changes immediately to blue and crystals suitable for X-ray crystallography appeared by slow evaporation at room temperature. Yield 0.17 g (11%). Found: C, 45.5; N, 4.0; H, 5.0; S, 9.1. Calc. for $Cu_2C_{26}H_{32}N_2S_2OCl_3$: C, 45.7; N, 4.1; H, 4.7; S, 9.4%.

X-Ray crystallography

A blue plate crystal (0.080 × 0.250 × 0.280 mm) was selected and mounted on a Rigaku AFC5S four-circle diffractometer. Unit cell parameters were determined from automatic centring of 25 independent reflections ($28.03° < 2\theta < 36.22°$) and refining the orientation matrix by least-squares. Intensities were collected at room temperature with graphite-monochromatized Mo K_α radiation, by using the ω–2θ scan technique, scan width 0.16°, and scan speed 4.0° min^{-1}; the intensities of three representative reflections which were measured after every 150 reflections declined by −0.70%. A linear correction factor was applied to the data to account for this phenomena. A total of 6888 independent reflections were measured to a maximum 2θ value of 55.0°; 6725 unique, R(int) = 0.031. The linear absorption coefficient for Mo K_α is 19.9 cm^{-1}. An empirical absorption correction, based on azimuthal scans of several reflections, was applied which resulted in transmission factors ranging from 0.75 to 1.00. The data were corrected for Lorentz and polarization effects.

Crystal data

Formula $Cu_4Cl_6S_4N_4C_{52}H_{64}O_2$, $f_w = 1372.24$, monoclinic, space group C2/c; $Z = 4$;

Table 1. Selected bond lengths (Å) and angles (°) with esds in parentheses for the $Cu_4Cl_6S_4N_4C_{52}H_{64}O_2$ molecule

Cu1—C11	2.296(1)	C4—C5	1.365(9)
Cu1—S1	2.337(1)	C5—C6	1.376(8)
Cu1—N1	2.026(4)	C6—C7	1.391(7)
Cu1—N2	2.020(4)	C7—C8	1.509(7)
Cu2A—Cu2B	0.596(5)	C9—C10	1.387(7)
Cu2A—Cl2	2.123(6)	C9—C14	1.407(7)
Cu2A—Cl3	2.132(6)	C10—C11	1.376(8)
Cu2B—Cl2	2.173(5)	C11—C12	1.370(9)
Cu2B—Cl3	2.523(5)	C12—C13	1.374(9)
Cu2B—Cl3	2.205(4)	C13—C14	1.391(7)
S1—C1	1.844(5)	C14—C15	1.509(7)
S1—C25	1.781(5)	C16—C17	1.517(8)
S2—C8	1.829(5)	C17—C18	1.520(8)
S2—C9	1.780(5)	C19—C20	1.501(7)
N1—C15	1.483(6)	C20—C21	1.402(7)
N1—C16	1.491(7)	C20—C25	1.405(7)
N2—C18	1.488(7)	C21—C22	1.366(8)
N2—C19	1.479(7)	C22—C23	1.375(9)
C1—C2	1.492(7)	C23—C24	1.392(8)
C2—C3	1.391(7)	C24—C25	1.374(7)
C2—C7	1.390(6)	O30—C31	1.348(9)
C3—C4	1.382(8)		

C11—Cu1—S1	83.98(5)	C11—Cu1—N2	176.1(1)
C11—Cu1—N1	92.7(1)	S1—Cu1—N2	95.5(1)
S1—Cu1—N2	89.0(2)	S2—C8—C7	107.9(3)
Cl2—Cu2A—Cl3	87.0(8)	S2—C9—C10	122.1(4)
Cl2—Cu2B—Cl3	121.3(1)	S2—C9—C14	118.1(4)
Cl3—Cu2B—Cl3	94.3(2)	C9—C14—C15	122.9(5)
Cu2B—Cl3—Cu2B	77.2(2)	N1—C15—C14	112.7(4)
Cu1—S1—C1	113.4(2)	N1—C16—C17	112.6(4)
Cu1—S1—C25	111.5(2)	C16—C17—C18	115.3(4)
C1—S1—C25	106.5(3)	N2—C18—C17	109.6(5)
C8—S2—C9	104.2(2)	N2—C19—C20	115.7(4)
Cu1—N1—C15	115.5(3)	C19—C20—C21	120.4(5)
Cu1—N1—C16	114.4(3)	C19—C20—C25	122.8(5)
C15—N1—C16	112.1(4)	S1—C25—C20	120.4(4)
Cu1—N2—C18	113.7(3)	S1—C25—C24	117.3(4)
Cu1—N2—C19	115.8(3)	S2—C8—C7	107.9(3)
C18—N2—C19	111.9(4)	S2—C9—C10	122.1(4)
S1—C1—C2	116.9(4)	S2—C9—C14	118.1(4)
C2—C7—C87	123.7(5)	C1—C2—C3	116.8(5)
C6—C7—C8	117.5(5)	C1—C2—C7	124.3(5)

$a = 24.357(3)$, $b = 11.368(3)$, $c = 20.737(4)$ Å, $\beta = 103.44(1)°$; $V = 5584(3)$ Å^3, calculated density 1.632 g cm^{-3}.

The structure was solved by direct methods[4] in the centrosymmetric space group C2/c. After anisotropic refinements of all non-hydrogen atoms, approximate positions of all hydrogen atoms, except that belonging to the hydroxyl group of the methanol molecule, could be picked from the subsequent difference Fourier map. Refinement of this atomic arrangement decreased the R value to 0.054 ($R_w = 0.054$). However, the refinements resulted in abnormal temperature factors for the copper atom of $[Cu_2Cl_4]^{2-}$ ($U_{11} = 0.053$, $U_{22} = 0.068$, $U_{33} = 0.214$, $U_{12} = 0.003$, $U_{13} = 0.027$, $U_{23} = 0.005$) indicating some disordering of the atom. After placing the copper in two close positions with fixed population parameters 0.5 and refining the structure, the R value decreased to 0.041 ($R_w = 0.042$). In the final refinements the non-hydrogen atoms were refined anisotropically and the hydrogen atoms, except those of the methanol molecule, were refined with fixed isotropic temperature factors. The final cycle of full-matrix least-squares refinement[5] was based on 3260 observed reflections ($I > 3.0\sigma$) and 418 variable parameters, and converged (largest parameter shift was 0.06 times its esd) with unweighted and weighted agreement factors of:

$$R = \Sigma||F_o| - |F_c||/\Sigma|F_o| = 0.041;$$

$$R_w = [(\Sigma w(|F_o| - |F_c|)^2/E_w F_o^2)]^{1/2} = 0.042.$$

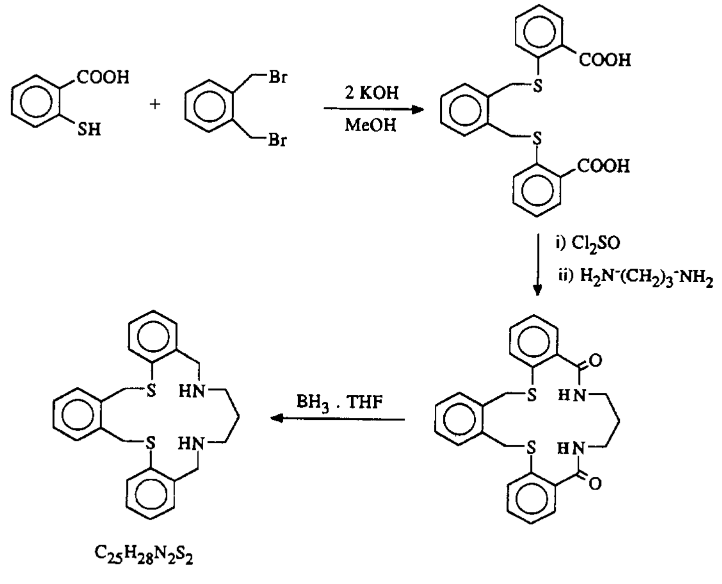
The standard deviation of an observation of unit weight[6] was 1.28. The weighting scheme was based on counting statistics and included a p-factor of 0.03 to downweight the intense reflections. Plots of $\Sigma w(|F_o| - |F_c|)^2$ vs $|F_o|$, reflection order in data collection, $\sin\theta/\lambda$, and various classes of indices showed no unusual trends. All calculations were done with TEXSAN software.[7] The maximum and minimum peaks on the final difference Fourier map correspond to 0.49 and -0.38 e Å^{-3}, respectively. After transformation the structure was also refined in the space group Cc. The refinements revealed similar disorder for the $[Cu_2Cl_4]^{2-}$ as in the centrosymmetric space group C2/c and did not decrease the R value. Therefore the final refinements have been carried out in the space group C2/c. Neutral atom scattering factors were taken from Cromer and Waber.[8] Anomalous dispersion effects were included in F_{calc}.[9] The values for $\Delta f'$ and $\Delta f''$ were those of Cromer.[10] Some bond lengths and angles are shown in Table 1.

RESULTS AND DISCUSSION

The new N_2S_2-type macrocycle 7,9-diaza-3,14-dithiatetracycle [15,4,0,0^{4,5},0^{13,14}] nonacosa-1(17),18,20,4(22),23,25,13(26),27,29-nonaene, was prepared according to the synthetic pathway shown in Scheme 1. By reaction of a methanolic solution of the macrocycle with $CuCl_2 \cdot 2H_2O$, a cubic, deep blue, air stable crystalline (cubic) complex was obtained of formula $[Cu(C_{25}H_{28}N_2S_2)Cl]_2\,[Cu_2Cl_4] \cdot 2CH_3OH$ (**3**). X-Ray diffraction analysis shows that it is an ionic compound containing both copper(II), $[Cu(C_{25}H_{28}N_2S_2)Cl]^+$, cations and copper(I), $[Cu_2Cl_4]^{2-}$, anions.

The $[Cu_2Cl_4]^{--}$ anion consists of two symmetry related $CuCl_2$ moieties bonded by two bridging chlorine ions (Fig. 1A). The whole symmetry of the dimer is C_2. The bond distances Cu2A—Cl3 and Cu2A—Cl3′ are not equivalent [2.132(5) Å and 2.678(6) Å]. Each copper(I) atom lies in a distorted, planar trigonal environment, but both planes containing the Cu^I ions are non-coplanar (136.02°). On the other hand, the metal atom occupies two close positions in the triangle Cl2, Cl3, Cl3′ (Cu2A... Cu2B distance, 0.596 Å). This observed crystallographic disorder could be explained by the existence of the enantiomeric pair in the crystal.

The non-equivalence of the Cu—Cl(bridging) bond distances permits one to consider the dimeric anion as a pair of strongly interacting monomer units, $CuCl_2^-$. The chlorocopper(I) complex anions have been reported in different ways. Linear monomeric units, $CuCl_2^-$, appear to be present in the salt tetrabutylammonium dichlorocuprate(I),[11] while planar dimeric, $[Cu_2Cl_4]^{2-}$, anions are present in $[VO(salen)(H_2O)][Cu_2Cl_4]^2$ and $[Cu_4(dmtp)_4Cl_2]$ $[Cu_2Cl_4]$.[3] The compound reported here represents the first example of a non-planar, dimeric conformation of the $[Cu_2Cl_4]^{2-}$ anion. Moreover,



Scheme 1.

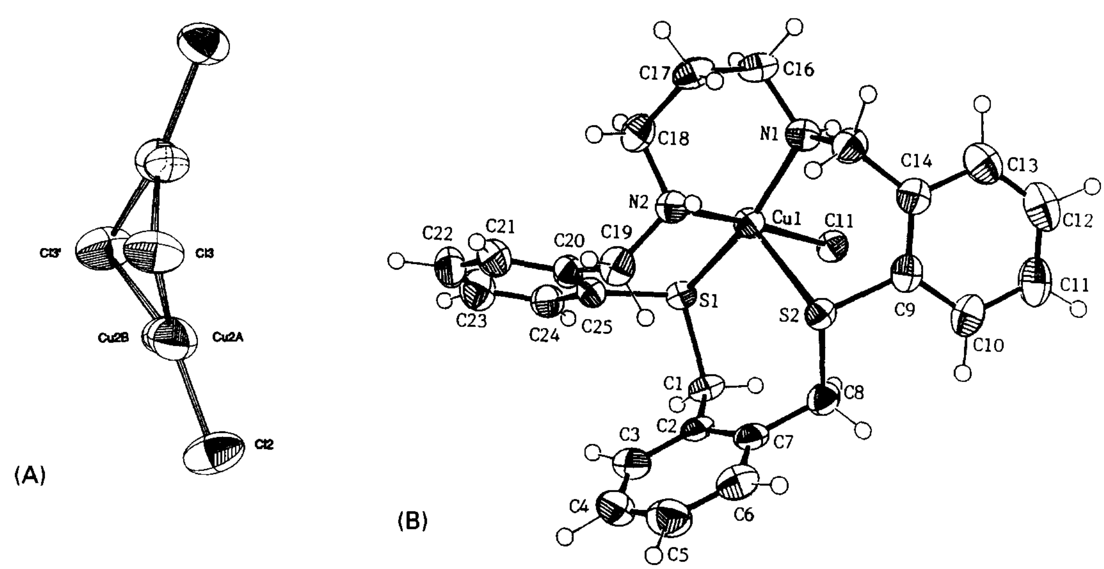


Fig. 1. Ortep drawing of (A) $[Cu_2Cl_4]^{2-}$ anion and (B) $[Cu(C_{25}H_{28}N_2S_2)Cl]^+$ cation, showing the atom-numbering scheme. The thermal ellipsoids are drawn at a 50% level.

the title compound can be considered as an intermediate case between the monomeric linear case $[CuCl_2]^-$ and the more symmetric, dimeric, planar, anionic group found in the compounds [VO(salen)$(H_2O)][Cu_2Cl_4]$ and $[Cu_4(dmtp)_4Cl_2][Cu_2Cl_4]$.

In the copper(II) counterion $[Cu(C_{25}H_{28}N_2S_2)Cl]^+$, the four short bonds provided by two N-atoms, one sulphur atom of the ligand and one chloride ion, form a distorted square planar environment to the metal atom (Fig. 1B) (distances from the mean plane defined by Cl1, N1, N2 and S1: Cl1, +0.0250 Å; N1, −0.3696 Å; N2, +0.3417 Å; S1, −0.0233 Å). The ligand's S2 sulphur atom provides an additional long fifth coordination to the metal ion (2.760 Å), so the Cu^{II} ion coordination environment could be considered a distorted square pyramid. The adopted non-planar molecular conformation of the macrocyclic ligand offers a closer tridimensional environment for the copper(II) ion, making it a bulky cation appropriate to stabilize the $[Cu_2Cl_4]^{2-}$ counterion.

The compound described here adds to the variety of conformational types exhibited by the $[Cu_2Cl_4]^{2-}$ copper(I) dimer. Up to now, the flexibility and well adapted structural features exhibited by this anion are quite intriguing.

Acknowledgements—This work was partially financed by "Comisión Interministerial de Ciencia y Tecnología (CICYT)" MAT91-0952 from the Spanish Government. R. K. is grateful to Suomen Kulttuurirahasto for a grant.

Supplementary Material Available—Listings of positional parameters for non-hydrogen and hydrogen atoms, anisotropic thermal parameters for non-hydrogen atoms, bond angles, torsion angles and bond lengths for hydrogen atoms (24 pages). Listing of observed and calculated structure factors (23 pages) can be obtained from the author on request.

REFERENCES

1. (a) M. Asplund, S. Jagner and M. Nilsson, *Acta Chem. Scand. A* 1982, **36**, 751; (b) M. Asplund and S. Jagner, *Acta Chem. Scand. A* 1984, **38**, 135; (c) M. Asplund and S. Jagner, *Acta Chem. Scand. A* 1984, **38**, 297.
2. L. Banzi, A. Bencini, A. Dei and D. Gatteschi, *Inorg. Chem. Acta* 1984, **84**, L11.
3. J. G. Haasnoot, T. L. F. Favre, W. Hinrichs and J. Reedijk, *Angew. Chem. Int. Ed. Engl.* 1988, **27**, 856.
4. (a) C. J. Gilmore, MITHRIL, An Integrated Direct Methods Computer Programs, *J. Appl. Cryst.* 1984, **17**, 42. University of Glasgow, Scotland; (b) P. T. Beurskens, DIRDIF, Direct Methods for Difference Structures. An automatic procedure for phase extension and refinement of difference structure factors. Technical Report 1984/1, Crystallography Laboratory, Toernooiveld, 6525 Ed Nijmegen, Netherlands.
5. Function minimized: $E_w(|F_o|-|F_c|)^2$; where $w = 4F_o^2/\sigma^2(F_o^2)$, $\sigma^2(F_o^2) = [S^2(C+R^2B)+pF_o^2)^2]/Lp^2$, S = scan rate, C = total integrated peak count, R = ratio of scan time to background counting time, B = total background count, Lp = Lorentz-polarization factor, p = p-factor.
6. Standard deviation of an observation of unit weight:

$[\Sigma w(|F_o|-|F_c|)^2/(N_o-N_v)]^{1/2}$; where N_o = number of observations, N_v = number of variables.

7. TEXSAN-TEXRAY: Structure Analysis Package, Molecular Structure Corporation, The Woodlands, TX (1985).
8. D. T. Cromer and J. T. Waber, *International Tables for X-ray Crystallography*, Vol. IV, Table 2.2A. The Kynoch Press, Birmingham, U.K. (1974).
9. J. A. Ibers and W. C. Hamilton, *Acta Cryst.* 1964, **17**, 781.
10. D. T. Cromer, *International Tables for X-ray Crystallography*, Vol. IV, Table 2.3.1. The Kynoch Press, Birmingham, U.K. (1974).
11. M. Asplund, S. Jagner and M. Nilsson, *Acta Chem. Scand. A* 1983, **37**, 57.