Inorganica Chimica Acta, 108 (1985) 11–15

The Preparation and Crystal Structure Analysis of a 2:1 Complex between L-lysine and Copper(II) Chloride

M. TERESA LEAL S. DUARTE, MARIA A. A. F. de C. T. CARRONDO, M. L. S. SIMÕES GONCALVES

Centro de Química Estrutural, Complexo I, IST, Lisbon, Portugal

M. B. HURSTHOUSE, N. P. C. WALKER and H. M. DAWES

Department of Chemistry, Queen Mary College, London, U.K.

Received March 21, 1985

Abstract

The crystal structure of bis(L-lysine)Cu(II) chloride dihydrate has been determined by X-ray analysis. The complex crystallizes in the monoclinic space group $P2_1$, with cell dimensions a = 5.189(1), b = 16.988(3), c = 11.482(2) Å, β = 93.57(1)°. The position of the Cu atom was found from a Patterson synthesis, the remaining atoms were located with DIRDIF. The structure was refined by least-squares to R = 0.060 and R_w = 0.065 for 2637 observed reflections. The copper(II) atom has an essentially square planar coordination with the two lysine molecules chelated via the carboxy oxygen and the α-amino nitrogen. However the two chlorine atoms form weak interactions with the metal to complete a strongly tetragonally elongated six-fold coordination. The two aliphatic chains have rather different geometries and are extended in a zig-zag mode. Extensive hydrogen bonding links the complex and the water molecules together.

Introduction

Aminoacids are good examples of model ligands in metal speciation studies. They provide a solid basis for carrying out further work with more complex natural ligand systems, as humic acids and polypeptides. Aminoacids can be present in coastal waters, regions with high level of phytoplancton, interstitial water of sediments and specially in some estuaries [1, 2].

On the other hand copper is an essential element which exists in some enzymes and may bound to certain aminoacids. It has been noticed that patients suffering from some inflammatory diseases have high contents of copper in their blood plasma. Furthermore a few anti-inflammatory drugs form strong complexes with metals, mainly with copper [3, 4].

Both fields suggest a careful study of aminoacid complexes with metals. Thus we undertook the study of the L-lysine complex with copper. The compound was synthesized, characterized by elemental analysis, infrared spectroscopy and its crystal structure was determined by X-ray diffraction.

Experimental

Preparation and Analysis of the Crystals

The crystals were prepared by a method described by de Meester and Hodgson [5]. 1 mmol of $CuCl_2$ (0.1346 g) dissolved in a minimum of water was added to 2 mmol of L-lysine monochlorohydrate (0.3653 g) dissolved in 20 ml of water. The pH was adjusted to 7 with NaOH (0.1 M), and some drops of ethanol added. Blue, very thin blade-like crystals appeared after a week at low temperature (4 °C). *Anal.*: Found C, 31.18; N, 12.01; H, 6.70; Cu, 12.7. Calculated for $C_{12}H_{32}N_4O_6Cu$: C, 31.13; N, 12.10; H, 6.98; Cu, 13.7. Copper was determined by Flame Atomic Absorption using a Perkin-Elmer Model 403.

Infrared Spectral Measurements

A Perkin-Elmer Model 683 spectrophotometer was used to obtain the infrared spectra of both complex and ligand dispersed in KBr pellets.

Crystallography

Data Collection

The crystal used for the X-ray work had dimensions of 0.35 × 0.1 × 0.1 mm. All X-ray measurements were made using an Enraf-Nonius CAD-4 diffractometer and graphite monochromatized Mo-K_α radiation ($\bar{\lambda}$ = 0.71069 Å). Cell dimensions were obtained by least-squares refinement of setting angles for 25 automatically centred reflections with $5.8° < \theta < 21.0°$.

0020-1693/85/$3.30

The intensities of 3341 independent reflections were measured via the $\omega/2\theta$ scan mode, with ω scan widths of $1.0 + 0.35 \tan\theta$ and scan speeds of 0.62–2.54 deg min^{-1}. The data were corrected for Lorentz and polarization effects but not for absorption.

Crystal Data

$C_{12}H_{32}N_4O_6Cl_2Cu$, M.W. = 462.92, monoclinic, space group $P2_1$, $a = 5.189(1)$, $b = 16.988(3)$, $c = 11.482(2)$ Å, $\beta = 93.57(1)°$, $V = 1010.3$ Å^3, $Z = 2$ $D_c = 1.51$ g cm^{-3}, $\mu(\text{Mo-K}_\alpha) = 12.3$ cm^{-1}.

Structure Determination

1983 data satisfied the criterium $I > 1.5\sigma(I)$ and were used for the structure solution and refinement. The position of the copper atom was found from a Patterson synthesis to be approximately 0.25, 0.25, 0.25. Although it proved possible to develop a recognisable structure from successive refinements and difference syntheses, starting with the copper phasing, the model obtained would not refine below $R \simeq 0.22$.

On the assumption that the x and z coordinates were likely to differ slightly from 0.25, analysis of possible solutions indicated that the nature of the off-setting from these idealised solutions was likely to be critical. Accordingly we selected one possibility with $x = 0.23$, $z = 0.247$ (the y coordinate was fixed at 0.25 to define the origin) and used the program DIRDIF [6] to develop the rest of the structure. This procedure was completely successful, all other non-hydrogen atoms being identified. The following refinement proceeded very smoothly giving an R value of 0.067, with all atoms assigned anisotropic thermal parameters. Hydrogen atoms were then inserted in idealised positions, and those on each specific carbon and nitrogen atom assigned an overall group isotropic thermal parameter. Further refinement, led to a final R $(=\Sigma\Delta F/\ \Sigma|F_o|)$ of 0.060 and R_w $(=(\Sigma w\Delta F^2/\Sigma w|F_o|^2)^{1/2})$ of 0.065. The weighting scheme $w = 1/|\sigma^2(F_o) + 0.0014\ F_o^2|$ gave satisfactory agreement analyses.

TABLE I. Fractional Atomic Co-ordinates (×10) for Cu(L-lysine)$_2$(Cl)$_2$·2H$_2$O.

	x	*y*	*z*
Cu	2407(3)	2500	2438(1)
Cl(1)	137(5)	3934(2)	3078(2)
Cl(2)	5291(5)	866(2)	1969(2)
O(11)	4179(14)	2996(5)	1179(6)
N(11)	−239(15)	2196(5)	1174(6)
C(11)	3217(17)	2797(6)	151(8)
O(12)	3919(16)	3103(6)	−746(6)
C(12)	1253(18)	2132(7)	110(8)
C(13)	−376(19)	2032(6)	−1018(7)
C(14)	−1903(19)	1279(6)	−1079(7)
C(15)	−3219(22)	1123(7)	−2265(9)
C(16)	−4829(20)	394(7)	−2288(8)
N(12)	−5900(20)	212(6)	−3497(8)
O(21)	725(13)	1938(4)	3655(6)
N(21)	5323(13)	2603(6)	3619(5)
C(21)	2017(16)	1857(5)	4611(7)
O(22)	1334(13)	1463(5)	5447(5)
C(22)	4632(16)	2295(5)	4766(6)
C(23)	4506(16)	2953(5)	5666(8)
C(24)	7219(17)	3262(5)	6057(7)
C(25)	7135(17)	3883(6)	6985(7)
C(26)	9839(17)	4166(6)	7357(7)
N(22)	9751(16)	4756(5)	8309(7)
Ow(1)	−2606(17)	428(5)	−5387(6)
Ow(2)	8266(21)	4075(6)	10354(8)

TABLE II. Anisotropic Temperature Factors[a] (Å ×10) for Cu(L-lysine)$_2$(Cl)$_2$·2H$_2$O.

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Cu	25(1)	56(1)	26	9(1)	−2	−13(1)
Cl(1)	40(1)	36(1)	48(1)	0(1)	9(1)	9(1)
Cl(2)	28(1)	28(1)	46(1)	4(1)	1(1)	0(1)
O(11)	26(3)	52(4)	33(3)	7(3)	1(3)	−12(3)
N(11)	21(3)	34(4)	26(3)	6(3)	7(3)	0(3)
C(11)	19(4)	48(6)	33(4)	16(4)	2(3)	6(4)
O(12)	38(4)	91(7)	37(4)	17(4)	9(3)	−19(4)
C(12)	21(4)	39(5)	29(4)	5(4)	4(3)	−9(4)
C(13)	32(5)	35(5)	20(3)	7(3)	−3(3)	−3(4)
C(14)	32(5)	36(5)	26(4)	4(3)	0(3)	−1(4)
C(15)	35(5)	42(5)	33(4)	−1(4)	2(4)	−9(4)
C(16)	28(5)	46(6)	32(4)	2(4)	4(3)	5(4)
N(12)	38(5)	47(5)	39(4)	−9(4)	5(4)	−12(4)
O(21)	26(3)	46(4)	28(3)	3(3)	0(2)	−10(3)
N(21)	23(3)	35(4)	24(3)	−9(3)	5(2)	−8(4)
C(21)	16(3)	23(4)	31(4)	−6(3)	2(3)	−4(3)
O(22)	32(4)	58(5)	26(3)	14(3)	3(3)	−12(3)
C(22)	16(3)	30(4)	21(3)	2(3)	1(3)	−6(3)
C(23)	21(4)	27(4)	30(4)	−7(3)	1(3)	−1(3)
C(24)	23(4)	31(5)	24(3)	−9(3)	2(3)	−4(3)
C(25)	19(4)	41(5)	30(4)	−7(4)	4(3)	−4(4)
C(26)	21(4)	39(5)	26(4)	0(3)	3(3)	−2(4)
N(22)	26(4)	32(4)	39(4)	−6(3)	−1(3)	0(3)
OW(1)	54(5)	41(4)	39(3)	3(3)	10(3)	−9(4)
OW(2)	62(6)	70(7)	70(6)	8(5)	10(5)	−25(5)

[a] The temperature factor exponent takes the form: $-2\pi(U \times h \times a^* + \ldots + 2U \times h \times k \times a^* \times b^*)$.

Atomic scattering factors were taken from International Tables [7] and the computations were carried out on a VAX 11/750 computer, using DIRDIF and SHELX 76 [8]. The drawings were made with SNOOPI [9] and ORTEP II [10].

Fractional atomic coordinates and anisotropic thermal parameters for the non-hydrogen atoms are listed in Tables I and II respectively. Tables of hydrogen fractional atomic coordinates and isotropic temperature factors and lists of observed and calculated structure factors are supplied as supplementary data.

TABLE III. Bond Lengths (A) and Angles (deg) for Cu(L-lysine)$_2$(Cl)$_2$·2H$_2$O.

Bond lengths			
Cl(1)–Cu	2.823(6)	O(11)–Cu	1.953(9)
N(11)–Cu	2.003(10)	O(21)–Cu	1.944(9)
N(21)–Cu	1.975(8)	C(11)–O(11)	1.298(12)
C(12)–N(11)	1.490(12)	O(12)–C(11)	1.228(12)
C(12)–C(11)	1.521(15)	C(13)–C(12)	1.512(13)
C(14)–C(13)	1.504(15)	C(15)–C(14)	1.509(14)
C(16)–C(15)	1.493(16)	N(12)–C(16)	1.496(13)
C(21)–O(21)	1.257(11)	C(22)–N(21)	1.482(11)
O(22)–C(21)	1.241(12)	C(22)–C(21)	1.548(13)
C(23)–C(22)	1.527(13)	C(24)–C(23)	1.543(14)
C(25)–C(24)	1.503(14)	C(26)–C(25)	1.519(14)
N(22)–C(26)	1.486(12)	Cl(2)–Cu	3.216
Bond angles			
O(11)–Cu–Cl(1)	92.5(4)	N(11)–Cu–Cl(1)	97.6(3)
N(11)–Cu–O(11)	84.7(4)	O(21)–Cu–Cl(1)	91.4(3)
O(21)–Cu–O(11)	176.1(4)	O(21)–Cu–N(11)	94.4(4)
N(21)–Cu–Cl(1)	93.4(4)	N(21)–Cu–O(11)	95.4(4)
N(21)–Cu–N(11)	169.0(4)	N(21)–Cu–O(21)	84.8(4)
O(11)–Cu–Cl(2)	90.2(4)	N(11)–Cu–Cl(2)	87.8(3)
O(21)–Cu–Cl(2)	86.1(4)	N(21)–Cu–Cl(2)	81.2(3)
C(11)–O(11)–Cu	112.9(7)	C(12)–N(11)–Cu	104.2(7)
O(12)–C(11)–O(11)	122.3(10)	C(12)–C(11)–O(11)	116.1(9)
C(12)–C(11)–O(12)	121.5(10)	C(11)–C(12)–N(11)	107.6(9)
C(13)–C(12)–N(11)	114.8(9)	C(13)–C(12)–C(11)	116.6(8)
C(14)–C(13)–C(12)	113.6(8)	C(15)–C(14)–C(13)	113.5(9)
C(16)–C(15)–C(14)	112.5(10)	N(12)–C(16)–C(15)	111.3(9)
C(21)–O(21)–Cu	116.2(7)	C(22)–N(21)–Cu	111.2(6)
O(22)–C(21)–O(21)	124.9(9)	C(22)–C(21)–O(21)	117.6(8)
C(22)–C(21)–O(22)	117.5(8)	C(21)–C(22)–N(21)	109.0(7)
C(23)–C(22)–N(21)	111.5(8)	C(23)–C(22)–C(21)	110.9(8)
C(24)–C(23)–C(22)	111.7(8)	C(25)–C(24)–C(23)	112.3(8)
C(26)–C(25)–C(24)	110.8(8)	N(22)–C(26)–C(25)	110.5(8)

Results and Discussion

Spectroscopic Studies

The structure of Cu(L-lysine)$_2$(Cl)$_2$·2H$_2$O was characterized by an infrared spectral analysis prior to the crystallographic study.

The spectra of both the complex and the free ligand exhibit the $-CH_2$ stretching vibration bands at about 2900 cm^{-1}, the scissor deformation ~1400 cm^{-1} and the $-CH_2$ wagging vibration in the region of 1300 cm^{-1}, commonly found for the aliphatic saturated hydrocarbon chain [11]. The symmetric and asymmetric NH$_2$ deformation bands appear in both spectra. The NH$_2$ stretching modes at ~3430, ~3240 and ~3130 cm^{-1} appear only in the complex spectrum. The complex formation is confirmed by the position of the –COO asymmetric stretching band since it moves from 1540 cm^{-1} in the free ligand, typical of a free carboxylate, to 1650 cm^{-1} in the complex indicating the covalent bonding with the copper [12]. The 950–200 cm^{-1} regions are identical with the exception of the bands at ~590 cm^{-1} and 270 cm^{-1} probably due to Cu–N and Cu–O asymmetric vibrations respectively [13].

Crystal Structure

The X-ray structure analysis shows that the copper atom has an essentially square-planar environment from the two chelating lysine molecules. However the two chloride atoms form weak interactions with the metal, to complete a strongly tetragonally elongated six-fold coordination.

A diagram of the structure is given in Fig. 1, bond lengths and angles are given in Table III.

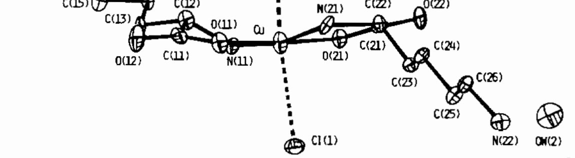

Fig. 1. Molecular diagram of the Cu(L-lysine)$_2$(Cl)$_2$·2H$_2$O with the two oxygens of the water molecules.

TABLE IV. Atom Deviations (Å) from the Least-squares Plane.

Atom[a]	Deviation (Å)	Atom[b]	Deviation (Å)	Atom[b]	Deviation (Å)
O(11)	0.062	Cu	0.128	Cl(2)	−3.081
N(11)	−0.063	Cl(1)	2.949	C(21)	−0.079
O(21)	0.064	C(11)	−0.304	O(22)	−0.246
N(21)	−0.063	O(12)	−0.288	C(22)	−0.012
		C(12)	−0.823	C(23)	1.245
		C(13)	−0.917		

[a] Atoms defining the plane. [b] Other atoms. [c] The equation of the square plane is given as $-2.366x + 14.611y + 2.949z = 3.674$ where x, y, z refer to the fractional coordinates.

Although no hydrogen atoms could be reliably located experimentally, we presume that the lysine molecules exist in the zwitterionic form with the carboxy protons transferred to the terminal ϵ-NH_2 groups. The aliphatic chains have an extended zig-zag conformation. The two lysine molecules chelate via the carboxy oxygen and the α-amino nitrogen, such that in the CuN_2O_2 equatorial group the oxygens are *trans* to each other. The Cu–N and Cu–O distances are very similar to those found in other copper–aminoacid structures [14–18]. The CuN_2O_2 group is significantly distorted from planarity and the geometry of the chelate rings show some significant differences.

The least-square plane of the four coordinating oxygen and nitrogen atoms shows a fairly even distortion of the shallow tetrahedral type with deviations of ±0.06 Å (see Table IV). The copper atom lies +0.128 out of the plane, in the same direction as the two oxygens and towards Cl(1) the chlorine which gives the slightly shorter Cu–Cl distance.

The differences in geometry of the chelate rings are best described in terms of selected torsion angles. These are listed in Table V, and show the marked deviation from planarity of the ring containing O(11) and N(11). Also noteworthy are the torsion angles involving C(13) and C(23) the first atoms of the side chains, which show the large difference in the orientation of the side chains, which show the large difference in the orientation of the side chains to the coordination plane. This feature is also apparent from the data in Table IV and from the diagrams and will be mentioned further below.

The Cu···Cl distances are much greater than the sum of covalent radii and the ‘in-plane’ Cu–Cl distances of 2.254(4), 2.293(4) Å found in the complex $CuCl_2$(L-histidine) [19], but are very similar to the axial contacts found in the histidine structure which link the molecules of this complex into chains. Thus whilst the chlorines in our structure must formally be regarded as chloride ions, there is clearly some Cl^-···Cu association. In fact these two interactions are part of a very extensive system of intermolecular interactions, mostly hydrogen bonds, linking the complex units, the chloride ‘ions’ and the water molecules together. In Table VI, we list interatomic distances which lie significantly below the sum of the relevant van der Waals contacts and which are considered to indicate interactions. The strongest interactions are also shown in Fig. 2. This intermolecular hydrogen bonds between the water molecules and the terminal $-NH_3^+$ groups and the carboxyl oxygens, together with bonds between Ow(2) and the coordinated O(11) atom and between the terminal N(12) and the carbonyl oxygen O(22) link the molecules into sheets perpendicular to *b*. Interactions between chlorine atoms and terminal

TABLE V. Torsion Angles (deg).

Cu–O(11)–C(11)–C(12)	−9.6
Cu–N(11)–C(12)–C(11)	−39.2
O(11)–C(11)–C(12)–N(11)	34.2
O(11)–C(11)–C(12)–C(13)	164.8
Cu–O(21)–C(21)–C(22)	7.3
Cu–N(21)–C(22)–C(21)	10.1
O(21)–C(21)–C(22)–N(21)	−11.6
O(21)–C(21)–C(22)–C(23)	111.4

TABLE VI. Hydrogen Bond Lengths.

Hydrogen Bonds X–H···Y	Interatomic Distances (Å) X···Y
OW(1)–H···N(12)	2.869
OW(1)–H···O(22a)	2.818
OW(2)–H···N(22)	2.770
OW(2)–H···O(11b)	3.001
OW(2)–H···O(12b)	3.010
N(12c)–H···O(22)	2.798
N(12)–H···Cl(1d)	3.148
N(22)–H···Cl(2e)	3.221

Symmetry code: (a) $x, y, -1.0 + z$, (b) $x, y, 1.0 + z$, (c) $1.0 + x, y, 1.0 + z$, (d) $-1.0 - x, -0.5 + y, -z$, (e) $2.0 - x, 0.5 + y, 1.0 - z$.

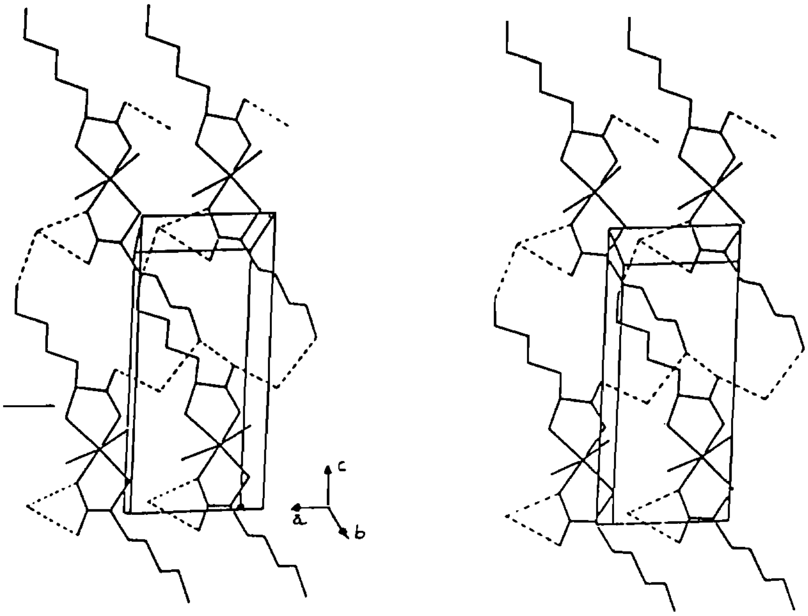

Fig. 2. A stereoscopic view in a direction almost parallel to the *b* axis showing the packing of the complex molecules and water molecules in the unit cell. The dashed lines represent the hydrogen bonds.

NH_3^+ groups then link the sheets to give a 3-Dimensional network. The interactions involving atoms in the two chelating ligands are different and this may be the cause of the great differences in chelate ring conformation and the side chain orientations.

Acknowledgements

We thank Professor Dr. Th. Hahn for the use of the CAD-4 diffractometer of the Rhein-Westf. Technische Hochschule in Aachen, F.R.G. This work was partially supported by the British Council and by Junta Nacional de Investigaçao Científica e Tecnológica under research contract No. 315.81.57.

References

1 W. Stumm and J. J. Morgan, in 'Aquatic Chemistry', Wiley, New York, 1970.
2 J. P. Riley and R. Chester, in 'Chemical Oceanography, Vol. VII, 2nd edn.', Academic Press, New York, 1978.
3 U. Weser, L. M. Schubotz and M. Younes, in J. O. Nriagu (ed.), 'Copper in the Envrionment, Part II', Wiley, New York, 1979, chap. 8.
4 U. Weser, E. Lengfelder, K.-H. Sellinger and L. Schobotz, in J. R. J. Sorenson (ed.), 'Inflammatory Diseases and Copper', Humana, New Jersey, 1982.
5 P. de Meester and D. J. Hodgson, *J. Am. Chem. Soc.*, *99*, 6884 (1974).
6 P. T. Beurskens, 'DIRDIF', Program for Direct Methods for Difference Structures, University of Nijegen, The Netherlands, 1983.
7 'International Tables for X-ray Crystallography, Vol. IV', Kynoch Press, Birmingham, 1974.
8 G. M. Sheldrick, 'SHELX 76', Crystallographic Calculations Program, University of Cambridge, 1976.
9 E. K. Davies, 'SNOOPI', Program for Plotting Crystal Structures, University of Oxford, 1983.
10 C. K. Johnson, 'ORTEP-II', Fortran Thermal-ellipsoid Plot Program for Crystal Illustrations, ORNL-5138, Oak Ridge National Laboratory, Tenn., 1976.
11 N. B. Colthup, L. H. Daly and S. E. Wiberley (eds.), 'Introduction to Infrared and Raman Spectroscopy', Academic Press, New York, 1964.
12 J. J. R. Fraústo da Silva and M. L. S. Simoes Gonçalves, *Rev. Port. Quím.*, *7*, 137 (1965).
13 Chia-Chih Ou, D. A. Powers, J. A. Thich, T. R. Felthouse, D. N. Hendrickson, J. A. Potenza and H. J. Schugar, *Inorg. Chem.*, *17*, 34 (1978).
14 T. G. Fawcet, M. Hushay, J. P. Rose, R. A. Lalancette, J. A. Potenza and H. J. Schugar, *Inorg. Chem.*, *18*, 327 (1979).
15 A. Dijkstra, *Acta Crystallogr.*, *20*, 588 (1966).
16 D. van der Helm and W. A. Franks, *Acta Crystallogr., Sect. B:*, *25*, 451 (1969).
17 J. A. Tich, D. Mastropaolo, J. Potenza and H. J. Schugar, *J. Am. Chem. Soc.*, *96*, 726 (1974).
18 C. W. Weeks, A. Cooper and D. A. Norton, *Acta Crystallogr., Sect. B:*, *25*, 443 (1969).
19 K. Golyvas, H. R. Tietze and S. K. J. Egri, *Aust. J. Chem.*, *35*, 1581 (1982).