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Heteronuclear, Mixed-nucleobase Complexes. 2. (μ-1-Methyluracilato-N^3,O^4)(μ-1-methylcytosine-N^3,O^2)-*cis*-diammineplatinum(II)·Silver Dinitrate·Silver Nitrate·2.5 Water

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Abstract

The preparation and crystal structure of a mixed 1-methyluracilato, 1-methylcytosine complex of composition *cis*-$[(NH_3)_2Pt(C_5H_5N_2O_2)(C_5H_7N_3O)Ag(OH_2)](NO_3)_2 \cdot AgNO_3 \cdot 2.5H_2O$ is described. The compound crystallizes in the triclinic system, space group $P\bar{1}$, with $a = 7.421(1)$, $b = 12.784(2)$, $c = 14.355(2)$ Å, $\alpha = 108.89(2)$, $\beta = 92.45(2)$, $\gamma = 105.22(1)°$, $Z = 1$. The structure was refined to $R = 0.050$ and $R_w = 0.046$ with use of 4327 independent reflections. Binding of the *cis*-$(NH_3)_2Pt^{II}$ moiety is through N3 of the uracil and N3 of the cytosine ring. One silver is directly coordinated to O4 of uracil and O2 of cytosine, leading to a Pt–Ag separation of 2.906(1) Å. Pairs of dinuclear Pt, Ag units are linked via aqua ligands and bridging nitrate ions to two additional silver ions which, in turn, complete their coordination spheres by an aqua ligand and a monodentate nitrate each. As a result, large 12-membered rings, consisting of four Ag ions, two H_2O groups, as well as two O–N–O bridges are formed. Ag–Ag distances in these rings vary between 3.553(1) and 6.898(1) Å.

Introduction

Uracil and thymine nucleobases, when platinated at the N3 position, display a pronounced tendency to bind additional metal (Pt or heterometal) ions via the adjacent exocyclic oxygens. The resulting complexes are numerous, differing in nuclearity, stoichiometry, and coordination geometry of the metals; for example ref. 1. As has been shown, this behaviour is neither restricted to Pt nor to uracil and thymine, but appears to be common also to other transition metals (Ag, Hg) of these or related cyclic amide ligands [2].

We have recently extended the variety of heteronuclear nucleobase complexes by an example containing different metals *and* different nucleobases [3]. In this compound, two *cis*-$[(NH_3)_2Pt(1\text{-MeU})(1\text{-MeC})]^+$ units (1-MeU = 1-methyluracil anion, 1-MeC = neutral 1-methylcytosine) are linked by a Cu(II) into a trinuclear complex of Pt_2,Cu-stoichiometry with rather short Pt–Cu distances of 2.681(1) Å. It was interesting to find O2 of the 1-MeC ligand so strongly involved in metal (Cu) binding, in addition to N3, which was bound to Pt. Using the same starting material, *cis*-$[(NH_3)_2Pt(1\text{-MeU})(1\text{-MeC})]NO_3$, and cocrystallizing it with $AgNO_3$, we have now isolated a complex of Pt,Ag_2-stoichiometry, which had some precedence in a complex of identical stoichiometry, derived from *trans*-$(NH_3)_2Pt(1\text{-MeU})_2$ [1i]. However, since 1-MeC and 1-MeU ligands differ in the exocyclic 4-position (NH_2 *vs.* O), we expected quite a different structure, as confirmed by the results of the crystal structure determination.

Experimental

The title compound, *cis*-$[(NH_3)_2Pt(1\text{-MeU})(1\text{-MeC})Ag(H_2O)](NO_3)_2 \cdot AgNO_3 \cdot 2.5H_2O$, was isolated as colorless, transparent crystals on slow evaporation (4 °C) of a filtered solution containing *cis*-$[(NH_3)_2Pt(1\text{-MeU})(1\text{-MeC})]NO_3$ [3] (0.25 mmol in 2 ml H_2O) and $AgNO_3$ (0.5 mol). Yield 67%. The crystals lose transparency in air due to loss of lattice water. Analysis of an air-dried sample: Calc. for $[(NH_3)_2Pt(C_5H_5N_2O_2)(C_5H_7N_3O)Ag(H_2O)](NO_3)_2 \cdot AgNO_3$: C, 13.36; H, 2.25; N, 15.58. Found: C, 13.10; H, 1.93; N, 15.23%.

The X-ray measurements were carried out at room temperature on a PHILIPS-PW 1100 single crystal diffractometer using graphite monochromated Mo Kα

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radiation ($\lambda = 0.71069$ Å). The crystal data are: size 0.05 × 0.05 × 0.15 mm, triclinic space group $P\bar{1}$, $a = 7.421(1)$, $b = 12.784(2)$, $c = 14.355(2)$ Å, $\alpha = 108.89(2)$, $\beta = 92.45(2)$, $\gamma = 105.22(1)°$, $U = 1231.1$ Å^3, $Z = 1$, $D_c = 2.490$ g cm^{-3}. A total of 4327 independent reflections were collected ($\theta/2\theta$ scans, $\theta_{max} = 25°$). Lp- and at a later stage empirical absorption corrections according to Walker and Stuart [4] ($\mu = 69.7$ cm^{-1}) were applied. For the calculations the set of 4152 reflections with $F_o > 2\sigma F_o$ was used.

The positions of the Pt and Ag atoms were determined by direct methods (Multan 84 [5]). The other non-hydrogen atoms were located by subsequent ΔF-syntheses. Hydrogen atoms were ignored during the structure determination. All atoms were refined with anisotropic thermal parameters. The final values for R and R_w are 0.050 and 0.046, respectively ($w^{-1} = \sigma^2(F) + 0.0001\ F^2$). In Table I the atomic coordinates and equivalent isotropic temperature factors (calculated by $U_{eq} = 1/3\ \Sigma U_{ij} a_i^* a_j^* a_i \cdot a_j$) are listed. Complex scattering factors were taken from refs. 6 and 7. Calculations were performed on a VAX 8600 computer using the SHELX program system [8].

TABLE I. Atomic Coordinates and Temperature Factors (Å^2) for the Pt,Ag$_2$ Complex

Atom	x	y	z	U
Pt1	0.7512(1)	0.0934(1)	0.3050(1)	0.027(1)
Ag1	0.5900(1)	0.2833(1)	0.3821(1)	0.047(1)
Ag2	1.2498(1)	0.4439(1)	0.6483(1)	0.087(1)
N10	1.0131(10)	0.2143(6)	0.3328(6)	0.036(7)
N11	0.7757(11)	0.0891(6)	0.4456(6)	0.040(7)
N1a	0.7062(13)	0.2006(8)	0.0552(6)	0.053(9)
C1a′	0.6876(24)	0.3098(13)	0.0430(12)	0.088(18)
C2a	0.7082(13)	0.1960(9)	0.1521(7)	0.040(9)
O2a′	0.6933(11)	0.2788(6)	0.2199(5)	0.053(7)
N3a	0.7285(10)	0.0944(7)	0.1627(6)	0.040(7)
C4a	0.7532(15)	0.0089(10)	0.0849(8)	0.047(10)
N4a′	0.7787(15)	−0.0824(8)	0.0996(7)	0.060(10)
C5a	0.7575(17)	0.0179(11)	−0.0123(9)	0.058(11)
C6a	0.7360(16)	0.1132(12)	−0.0223(8)	0.059(12)
N1b	0.3092(12)	−0.2152(7)	0.2611(7)	0.047(8)
C1b′	0.3027(19)	−0.3376(10)	0.2413(11)	0.072(14)
C2b	0.4814(14)	−0.1375(8)	0.2658(7)	0.039(9)
O2b′	0.6232(10)	−0.1705(5)	0.2505(6)	0.051(7)
N3b	0.4937(10)	-0.0242(6)	0.2823(5)	0.034(7)
C4b	0.3300(12)	0.0132(9)	0.2937(7)	0.040(9)
O4b′	0.3381(9)	0.1147(6)	0.3045(6)	0.049(7)
C5b	0.1583(15)	−0.0704(9)	0.2934(8)	0.050(10)
C6b	0.1533(15)	−0.1785(9)	0.2779(9)	0.052(11)
N20	1.3219(13)	0.1918(8)	0.5309(7)	0.049(9)
O20	1.4393(12)	0.1386(8)	0.5266(6)	0.071(9)
O21	1.1619(11)	0.1452(8)	0.5435(7)	0.074(10)
O22	1.3603(16)	0.2893(7)	0.5241(8)	0.088(12)
N30	0.8816(13)	0.4447(7)	0.5657(7)	0.049(8)
O30	0.9775(12)	0.5241(7)	0.6400(6)	0.068(8)
O31	0.7445(12)	0.4611(7)	0.5234(6)	0.068(9)
O32	0.9193(12)	0.3532(6)	0.5355(7)	0.074(9)
N40	0.2009(21)	0.3119(13)	0.1084(11)	0.087(15)
O40	0.1775(25)	0.2349(13)	0.1419(12)	0.149(22)
O41	0.1588(21)	0.2949(11)	0.0197(9)	0.123(17)
O42	0.2674(36)	0.4096(13)	0.1617(13)	0.242(42)
O50	0.4510(10)	0.4255(6)	0.3407(6)	0.059(8)
O51	1.2686(13)	0.3745(7)	0.7837(7)	0.078(10)
O52	0.4141(69)	0.4763(22)	0.9711(18)	0.205(77)

Results and Discussion

cis-(NH$_3$)$_2$Pt^{II} is coordinated to the anionic 1-MeU ligand and to the neutral 1-MeC ligand through N(3) each. The differentiation of 1-MeU and 1-MeC ligands, which is not straightforward on crystallographic arguments, is based on chemical-sense arguments, as outlined before [3]. Accordingly, Ag(1) is bound via the exocyclic O(4b′) of 1-MeU and the exocyclic O(2a′) oxygen of 1-MeC. It completes its strongly distorted tetrahedral coordination sphere by a water molecule, O(50), and the oxygen O(31) of a nitrate group (Fig. 1). Both the water molecule O(50) and the nitrate group binding to Ag(1) act as bridges to the second silver atom, Ag(2) (Fig. 2). Ag(2), in turn, completes its coordination sphere by

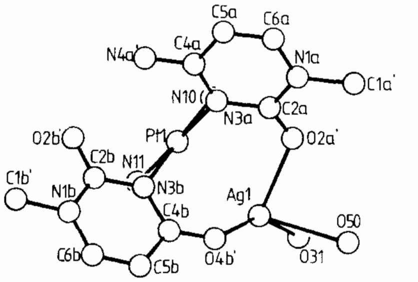

Fig. 1. Molecular cation of the title compound *cis*-[(NH$_3$)$_2$-Pt(1-MeU)(1-MeC)Ag(OH$_2$)(ONO$_2$)]$^+$. Of the coordinating nitrate, only the oxygen (O31) is shown.

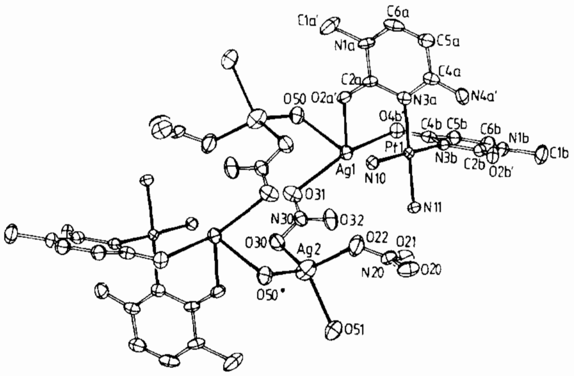

Fig. 2. View of the centrosymmetric arrangement of two Pt, Ag units, linked by two additional Ag ions. The ionic nitrate (N40, O40, O41, O42) and the water molecule O52 (half occupancy) are omitted for clarity.

TABLE II. Interatomic Distances (Å) and Angles (deg) around the Metals

Pt1–N10	2.069(7)	N10–Pt1–N11	92.0(3)
Pt1–N11	2.039(10)	N10–Pt1–N3a	88.2(3)
Pt1–N3a	2.046(10)	N10–Pt1–N3b	178.2(3)
Pt1–N3b	2.037(7)	N11–Pt1–N3a	178.7(4)
		N11–Pt1–N3b	86.3(3)
		N3a–Pt1–N3b	93.5(3)
Ag1–O4b′	2.352(6)	O4b′–Ag1–O2a′	91.1(3)
Ag1–O2a′	2.470(8)	O4b′–Ag1–O50	98.5(3)
Ag1–O50	2.521(10)	O4b′–Ag1–O31	151.6(3)
Ag1–O31	2.459(7)	O2a′–Ag1–O50	77.2(3)
		O2a′–Ag1–O31	115.5(3)
		O50–Ag1–O31	79.1(3)
Ag2–O22	2.540(11)	O22–Ag2–O51	96.2(4)
Ag2–O51	2.396(13)	O22–Ag2–O50*	87.5(4)
Ag2–O50*	2.366(10)	O22–Ag2–O30	133.3(3)
Ag2–O30	2.509(10)	O51–Ag2–O50*	106.4(3)
		O51–Ag2–O30	114.0(4)
		O50*–Ag2–O30	114.6(3)

a terminal aqua ligand, O(51), and a nitrate oxygen, O(22). Some of the angles about Ag(2) deviate markedly from an ideal tetrahedral coordination geometry (Table II), but clearly, deviations are not as large as for Ag(1). Ag–O distances are in the normal range (2.35(1)–2.54(1) Å).

The square-planar coordination geometry of Pt is normal. As can be seen from Fig. 1, the Pt plane and the plane defined by O(2a′), O(4b′), and Ag(1) are substantially tilted toward each other (23.5°), leading to a Pt–Ag(1) separation of 2.906(1) Å. This value compares with Pt–Ag distances of 2.849(1)–2.896(3) Å in related heteronuclear complexes containing uracil or thymine bridges [1b, 1i, 1j] and 2.772(3)–3.063(3) Å in two chloro-bridged (Pt, Ag)$_n$ (n = 1, 2) complexes [9].

The arrangement of two centrosymmetrically related Pt,Ag$_2$ units in the title compound is quite interesting in that the four Ag atoms, Ag(1), Ag(2), Ag(1*), and Ag(2*), are part of a 12-membered macrocycle, with four nitrate oxygens, O(31), O(31*), O(30), O(30*), two nitrate nitrogens, N(30), N(30*), and the bridging water oxygens, O(50), O(50*), being the other ring atoms (Fig. 3). Within the metallacycle, the respective intermetallic distances are 3.553(1) Å for Ag(1)–Ag(2*), 5.553(2) Å for Ag(1)–Ag(2), and 6.898(1) Å for Ag(1)–Ag(1*). Even the shortest of these distances is still considerably longer than the 2.994(6) Å Ag–Ag separation in the above-mentioned $Pt_2Ag_2Cl_4L_4$ ($L = C_6F_5$) complex [9] which has been interpreted as representing a Ag–Ag bond. It is somewhat surprising that aqua ligands rather than nitrate oxygens (e.g. O(40), O(41), or O(42) from the ionic nitrate) are utilized in bridging Ag(1) and Ag(2*). However, as indicated in Fig. 3, this nitrate group forms a 79° angle with the plane defined by Ag(1), Ag(2*), and O(50), thus enabling hydrogen bonding between the two protons of the aqua ligand and the nitrate oxygens O(42) (2.78 Å) and O(40) (3.26 Å).

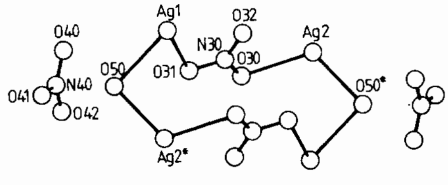

Fig. 3. Section of Fig. 2, indicating the 12-membered ring formed by the four Ag ions, two aqua ligands, and two nitrates. The capping ionic nitrates are involved in hydrogen bonding with the aqua bridges O50 and O50*.

Interatomic distances and angles within the heterocyclic rings and of the nitrates are given in Table III. Due to the relatively large errors, a detailed discussion is not meaningful. In particular, no differences in nitrate geometries can be seen, despite the fact that three different types of nitrates are present, with one being 'free', one coordinating in a unidentate fashion, and one acting in a bridging (anti-anti [10]) manner.

Selected conformational parameters are listed in Table IV, and possible hydrogen bonds are given

TABLE III. Interatomic Distances (Å) and Angles (deg) within 1-MeC (a), 1-MeU (b) and Nitrates

N1a–C1a′	1.50(2)	C6a–N1a–C2a	121(1)
N1a–C2a	1.41(2)	N1a–C2a–N3a	116(1)
C2a–O2a′	1.22(1)	C2a–N3a–C4a	121(1)
C2a–N3a	1.40(2)	N3a–C4a–C5a	121(1)
N3a–C4a	1.35(1)	C4a–C5a–C6a	117(1)
C4a–N4a′	1.31(2)	C5a–C6a–N1a	123(1)
C4a–C5a	1.44(2)		
C5a–C6a	1.32(2)		
C6a–N1a	1.37(2)		
N1b–C1b′	1.48(2)	C6b–N1b–C2b	120(1)
N1b–C2b	1.38(1)	N1b–C2b–N3b	120(1)
C2b–O2b′	1.24(1)	C2b–N3b–C4b	120(1)
C2b–N3b	1.37(1)	N3b–C4b–C5b	117(1)
N3b–C4b	1.41(1)	C4b–C5b–C6b	121(1)
C4b–O4b′	1.24(2)	C5b–C6b–N1b	122(1)
C4b–C5b	1.43(1)		
C5b–C6b	1.32(2)		
C6b–N1b	1.36(2)		
N20–O20	1.23(2)	O20–N20–O21	117(1)
N20–O21	1.23(1)	O20–N20–O22	123(1)
N20–O22	1.24(2)	O21–N20–O22	120(1)
N30–O30	1.24(1)	O30–N30–O31	118(1)
N30–O31	1.26(2)	O30–N30–O32	120(1)
N30–O32	1.22(1)	O31–N30–O32	122(1)
N40–O40	1.21(3)	O40–N40–O41	123(1)
N40–O41	1.23(2)	O40–N40–O42	120(2)
N40–O42	1.19(2)	O41–N40–O42	117(2)

TABLE IV. Conformational Parameters

(a) Deviations (in A) of atoms from best planes[a]					
(I) Pt1 coordination plane					
N10(*)	N11(*)	N3a(*)	N3b(*)	Pt1	
−0.02	0.02	0.02	−0.02	−0.01	
(II) plane through Ag1					
Ag1(*)	O2a′(*)	O4b′(*)	O31	O50	
0.0	0.0	0.0	−0.40	−2.43	
(III) 1-MeC plane					
N1a(*)	C2a(*)	N3a(*)	C4a(*)	C5a(*)	C6a(*)
−0.02	0.02	−0.01	−0.01	0.00	0.01
C1a′	O2a′	N4a′	Pt1	Ag1	
0.03	0.08	0.02	0.20	−0.55	
(IV) 1-MeU plane					
N1b(*)	C2b(*)	N3b(*)	C4b(*)	C5b(*)	C6b(*)
−0.03	0.01	0.02	−0.03	0.01	0.01
C1b′	O2b′	O4b′	Pt1	Ag1	
−0.05	−0.03	−0.08	0.28	0.84	
(b) Dihedral angles (in deg)					
I/II	23.5	I/III	73.2	I/IV	97.5
II/III	61.4	II/IV	75.0	III/IV	75.9

[a] Atoms with (*) define the plane; equations of planes refer to the *abc* basis.

(I) $4.980x - 10.628y - 1.031z = 2.440$ A

(II) $5.722x - 10.357y + 3.931z = 1.944$ A

(III) $6.701x + 1.617y + 0.350z = 5.097$ A

(IV) $0.756x - 2.054y + 13.876z = 4.324$ A

in Table V. As to hydrogen bonding interactions other than the ones already mentioned, hydrogen bonding within the Pt(1),Ag(1) cation occurs between the exocyclic amino group N(4a′) of 1-MeC and the exocyclic keto oxygen O(2b′) of the 1-MeU ring, as is the case in the related trinuclear Pt_2,Cu complex [3]. Intermolecular hydrogen bonding takes place between the NH_3 groups of Pt and various nitrate oxygens, between the water ligand O(51) and O(2b′) of 1-MeU, between O(51) and the lattice water O(52), and finally between the lattice water and nitrate oxygens O(41) and O(42).

In summary, the heteronuclear complex described here further exemplifies the chelating qualities of exocyclic groups of nucleobases (and in particular of uracil bases) held in proper register by a *cis*-$(NH_3)_2Pt^{II}$ moiety. The dinuclear Pt,M (M = heterometal) structure is retained even in conditions of excess heterometal, and an alternative arrangement with the two nucleobases individually binding one heterometal each is not realized.

TABLE V. Possible Hydrogen Bonding Interactions (Distances in A, Angles in deg)

N4a′–O2b′	2.90	C4a–N4a′–O2b′	124
N10–O22	3.39	Pt1–N10–O22	128
N10–O32	3.10	Pt1–N10–O32	90
N11–O21	2.94	Pt1–N11–O21	116
O40–O50	3.26	N40 O40–O50	87
O42–O50	2.78	N40–O42–O50	112
N11–O20(i)	2.93	Pt1–N11–O20(i)	106
O41–O52(ii)	2.88	N40–O41–O52(ii)	108
O42–O52(ii)	3.27	N40–O42–O52(ii)	89
N10–O4b′(iii)	2.99	Pt1–N10–O4b′(iii)	115
N10–O40(iii)	3.11	Pt1–N10–O40(iii)	114
O51–O52(iii)	2.62	Ag2–O51–O(52(iii)	133
N4a′–O41(iv)	2.87	C4a–N4a′–O41(iv)	136
O31–O50(v)	2.74	N30–O31–O50(v)	111
O2b′–O51(vi)	2.83	C2b–O2b′–O51(vi)	139
N11–O20(vi)	3.09	Pt1–N11–O20(vi)	117
N11–O21(vi)	3.20	Pt1–N11–O21(vi)	114
N10–O30(vii)	3.22	Pt1–N10–O30(vii)	117
O22–O50(vii)	3.40	N20–O22–O50(vii)	142

Symmetry transformations

(i) $= -1 + x, y, z$
(ii) $= x, y, -1 + z$
(iii) $= 1 + x, y, z$
(iv) $= 1 - x, -y, -z$
(v) $= 1 - x, 1 - y, 1 - z$
(vi) $= 2 - x, -y, 1 - z$
(vii) $= 2 - x, 1 - y, 1 - z$

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References

1 (a) B. Lippert, D. Neugebauer and U. Schubert, *Inorg. Chim. Acta, 46,* L11 (1980); (b) B. Lippert and D. Neugebauer, *Inorg. Chim. Acta, 46,* 171 (1980); (c) B. Lippert and U. Schubert, *Inorg. Chim. Acta, 56,* 15 (1981); (d) B. Lippert and D. Neugebauer, *Inorg. Chem., 21,* 451 (1982); (e) D. M. L. Goodgame, R. W. Rollins and B. Lippert, *Inorg. Chim. Acta, 66,* L59 (1982); (f) D. Neugebauer and B. Lippert, *Inorg. Chim. Acta, 67,* 151 (1982); (g) D. Neugebauer and B. Lippert, *J. Am. Chem. Soc., 104,* 6596 (1982); (h) B. Lippert, D. Neugebauer and G. Raudaschl, *Inorg. Chim. Acta, 78,* 161 (1983); (i) H. Schöllhorn, U. Thewalt and B. Lippert, *J. Chem. Soc., Chem. Commun.,* 769 (1984); (j) U. Thewalt, D. Neugebauer and B. Lippert, *Inorg. Chem., 23,* 1713 (1984); (k) H. Schöllhorn, U. Thewalt and B. Lippert, *Inorg. Chim. Acta, 93,* 19 (1984); (l) D. M. L. Goodgame, R. W. Rollins and B. Lippert, *Polyhedron, 4,* 829 (1985); (m) H. Schöllhorn, U. Thewalt and B. Lippert, *Inorg. Chim. Acta, 108,* 77 (1985).

2 (a) J. Perron and A. L. Beauchamp, *Inorg. Chem.*, *23*, 2853 (1984) and references cited therein; (b) F. Guay and A. L. Beauchamp, *Inorg. Chim. Acta*, *66*, 57 (1982).

3 B. Lippert, U. Thewalt, H. Schöllhorn, D. M. L. Goodgame and R. W. Rollins, *Inorg. Chem.*, *23*, 2807 (1984).

4 N. Walker and D. Stuart, *Acta Crystallogr., Sect. A*, *39*, 158 (1983).

5 P. Main, G. Germain and M. M. Woolfson, 'MULTAN', University of York, York.

6 D. T. Cromer and J. B. Mann, *Acta Crystallogr., Sect. A*, *24*, 321 (1968).

7 D. T. Cromer and D. Liberman, *J. Chem. Phys.*, *53*, 1891 (1970).

8 G. M. Sheldrick, 'SHELX-76', Program System, University of Cambridge, 1976.

9 R. Uson, J. Forniés, B. Menjón, F. A. Cotton, L. R. Falvello and M. Tomás, *Inorg. Chem.*, *24*, 4651 (1985).

10 C. C. Addison, N. Logan and S. C. Wallwork, *Q. Rev.*, *25*, 289 (1971).