Inorganica Chimica Acta, 110 (1985) 205–210

Preparation and Characterization of some Uranyl Complexes of Amino Acids. The Crystal Structure of $[UO_2(\gamma\text{-Aminobutanoic Acid})_3](NO_3)_2$

A. BISMONDO, U. CASELLATO, S. SITRAN

Istituto di Chimica e Tecnologia dei Radioelementi, C.N.R., Corso Stati Uniti, 35100 Padua, Italy

and R. GRAZIANI

Istituto di Chimica Generale, Università di Padova, 35100 Padua, Italy

Received March 27, 1985

Abstract

Uranyl complexes of glycine, β-alanine and γ-aminobutanoic acid were prepared and characterized. All those studied or examined contain the aminoacids in the zwitterionic form binding the metal through the ionized carboxyl group. The structure of the title compound was determined by X-ray crystallography and refined to $R = 6.6\%$. The crystals are triclinic, space group $P1$, $Z = 2$, with $a = 11.966(5)$, $b = 12.054(5)$, $c = 10.581(5)$ Å, $\alpha = 70.88(3)^\circ$, $\beta = 109.89(3)^\circ$, and $\gamma = 120.72(3)^\circ$. The uranyl group is equatorially bonded to the bidentate carboxylate of three molecules of the organic ligand forming a distorted hexagonal bipyramidal coordination geometry around the metal. U–O(equatorial) distances are in the range 2.24–2.48 Å.

Introduction

The interaction of the UO_2^{2+} ion with alpha, beta, or gamma-amino acids has largely been investigated with particular attention to the determination of the stability constants of the resulting complexes. In principle the coordination of this ion to simple amino acids can be achieved through the nitrogen atom of the amino group and, or, through the carboxyl oxygen atoms. Potentiometric and calorimetric data on UO_2^{2+} complexes with glycine, β-alanine, and γ-aminobutanoic acid [1, 2] show that in water solution, at pH 2 to 4 in order to avoid hydrolysis, the ligand binds through the carboxylic group, whereas the protonation of the amino nitrogen atom prevents any chelation.

With the aim to correlate the behaviour of these compounds in solution and in the solid, uranyl complexes with glycine, β-alanine, and γ-aminobutanoic acid were isolated from perchlorate or nitrate solutions.

We report here the synthesis of these complexes and the crystal structure of tris(γ-aminobutanoic acid)dioxouranium(VI) dinitrate.

Experimental

Compounds

Uranyl perchlorate was prepared by a standard method [3]. Uranyl nitrate was a commercial product, used without further purification. The aminoacids (HL) used:

glycine(HL^1)	$^+NH_3-CH_2-COO^-$
β-alanine (HL^2)	$^+NH_3-(CH_2)_2-COO^-$
γ-aminobutanoic acid (HL^3)	$^+NH_3-(CH_2)_3-COO^-$

were purified from an $EtOH/H_2O$ mixture and dried at 110–120 °C. The reactions were all carried out in aqueous solution, in different molar ratios (UO_2: HL = 1:1, 1:2, 1:3) and the products were isolated by slow evaporation of the solvent. In any case the composition of the compounds (Table I) was independent of the molar ratio used.

It is noticeable that only monoligand complexes were obtained with glycine and β-alanine, and only tris complexes with the γ-aminobutanoic acid. The IR spectra were examined in the range 4000–400 cm^{-1} (Table II). Two intense bands in the 1450–1600 cm^{-1} region are characteristic for the ionic carboxylic group; a single broad band in the 3260–3100 cm^{-1} region and another one in the 1600–1650 cm^{-1} region are associated with the presence of protonated amino group [4].

The thermal analysis of **IV** (Fig. 1) was made using a NETZSCH STA429 thermoanaliser in a dynamic nitrogen atmopshere (200 ml/min) and a heating rate of 2 °C min^{-1}. The sample was heated to 1200 °C

0020-1693/85/$3.30

TABLE I. Elemental Analysis.

$[UO_2(OH)HL^1]ClO_4 \cdot 3H_2O$, **I**
Calcd.: C, 4.7; H, 2.3; Cl, 6.9; N, 2.7; mol. wgt. 515.5
Found: C, 4.5; H, 1.4; Cl, 6.5; N, 2.3.

$[UO_2(OH)HL^2]ClO_4 \cdot 3H_2O$, **II**
Calcd.: C, 6.8; H, 2.6; Cl, 6.7; N, 2.6; mol. wgt. 529.5
Found: C, 6.6; H, 2.0; Cl, 6.4; N, 2.5.

$[UO_2(HL^3)_3](ClO_4)_2$, **III**
Calcd.: C, 18.5; H, 3.5; Cl, 9.1; N, 5.4; mol. wgt. 778
Found: C, 18.4; H, 3.3; Cl, 9.4; N, 5.3

$[UO_2(HL^3)_3](NO_3)_2 \cdot H_2O$, **IV**
Calcd.: C, 20.0; H, 4.0; N, 9.7; mol. wgt. 721
Found: C, 19.7; H, 3.8; N, 9.5

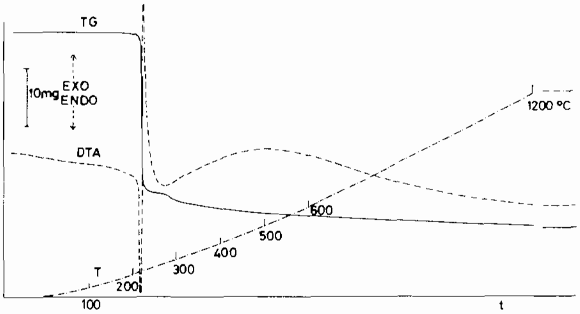


Fig. 1. Thermal analysis of **IV**.

using inactive Al_2O_3 as reference material and the temperature was then held until the weight was constant and corresponding to UO_2.

There was complete agreement between the found and required loss of weight. The DTA curve shows two very close endothermic peaks immediately followed by an exothermic one.

X-ray Data

A small fragment of the compound $[UO_2(HL^3)_3] \cdot (NO_3)_2 \cdot H_2O)$ (complex **IV**) (maximum dimension 0.2 mm) was used for the X-ray work. Crystal data are $C_{12}H_{27}N_5O_{14}U + H_2O$, $F_w = 703 + 18$, $a = 11.966(5)$, $b = 12.054(5)$, $c = 10.581(5)$ Å, $\alpha = 70.88(3)°$, $\beta = 109.89(3)°$, $\gamma = 120.72(3)°$, $V = 1211$ Å^3, $D_x = 1.98$ g cm^{-3} for $Z = 2$, (Mo Kα) = 98.5 cm^{-1}; triclinic space group $P1$, general positions $\pm(x,y,z)$. Intensity data were measured on a Philips diffractometer with the $\theta-2\theta$ scan technique up to $\theta = 25°$ using the Mo Kα radiation. Reference reflexions recorded at regular intervals during the data collection showed no significant change in intensity. The 4082 recorded intensities were corrected for Lp and for absorption [5] and 3410 with $I > 3\sigma(I)$ were used in subsequent calculations. The structure was solved by the heavy atom method and refined by least-squares to the final conventional R of 6.6%. The quantity minimized in the refinement was $\Sigma w(\Delta F)^2$ with $w = 1$. A final Fourier difference map showed no significant feature, apart from some residual electron density around the uranium position. Scattering factors for U were those of International Tables for X-ray Crystallography, 1974; those for N, O, and C were supplied internally by SHELX-76 [6]. A correction for the anomalous dispersion of U was applied [7]. Positional and thermal parameters are given in Table III, distances and angles in Table IV.

Results and Discussion

As shown in Figs. 2 and 3, the structure of the compound consists of $[UO_2(H_3N^{(+)}-(CH_2)_2-COO^{(-)})_3]^{++}$ cations in which the uranyl groups are six-coordinated by three acid molecules giving approximately hexagonal bipyramidal geometry about the uranium atom, and NO_3^- anions. Each ligand molecule is a zwitterion with the ionized carboxyl chelated to the metal and the amino terminus protonated. The six equatorial oxygen atoms are alternatively displaced [O(3) −0.04, O(4) 0.06, O(5) −0.05, O(6) 0.02, O(7) 0.01, O(8) 0.00, U −0.03 Å] from the L.S. mean plane of equation $-0.0366\ X - 0.0096\ Y - 0.9993\ Z = -1.726$ Å in

TABLE II. Main Infrared Bands (cm^{-1}) of the Prepared Complexes.

Compound	$\nu_{-NH_3^+}$ stretching and deformation	$\nu_{asymm\ COO^-}$	$\nu_{symm\ COO^-}$	ClO_4^- or NO_3^- bands	$\nu_3 OUO$
$[UO_2(OH)HL^1]ClO_4 \cdot 3H_2O$	3260 1630	1580	1460	1100 630	930
$[UO_2(OH)HL^2]ClO_4 \cdot 3H_2O$	3120 1610	1550	1450	1100 650	900
$[UO_2(HL^3)_3](ClO_4)_2$	3160 1620	1530	1455	1100 625	920
$[UO_2(HL^3)_3](NO_3)_2 \cdot H_2O$	3140 1640	1530	1455	1380	920

TABLE IIIa. Atomic Coordinates with e.s.d.s in Parentheses.

Atom	*x/a*	*y/b*	*z/c*
U(1)	0.2072(1)	0.3071(1)	0.1768(1)
O(1)	0.1625(10)	0.3321(15)	−0.0059(15)
O(2)	0.2491(15)	0.2758(13)	0.3605(12)
O(3)	0.0623(11)	0.0715(11)	0.1813(17)
O(4)	0.2623(10)	0.1414(10)	0.1621(15)
O(5)	0.4436(10)	0.4010(11)	0.1692(15)
O(6)	0.3749(11)	0.5386(11)	0.1672(15)
O(7)	0.1185(11)	0.4508(11)	0.1780(15)
O(8)	−0.0236(11)	0.2451(11)	0.1834(15)
O(9)	0.5636(17)	0.9312(16)	0.3227(19)
O(10)	0.4702(23)	0.8086(23)	0.4891(22)
O(11)	0.6459(36)	0.9818(22)	0.5186(28)
N(1)	0.2970(17)	−0.2888(16)	0.2328(23)
N(2)	0.8118(20)	0.9599(18)	0.2735(28)
N(3)	−0.4588(18)	0.1957(16)	0.2401(19)
N(4)	0.5641(26)	0.9073(20)	0.4429(24)
N(5)	0.5	0.0	0.0
O(12)[a]	0.5262(80)	0.1100(44)	−0.0009(49)
O(13)[a]	0.5555(88)	−0.0407(88)	−0.0305(68)
O(14)[a]	0.3840(47)	−0.0735(89)	−0.0100(54)
O(15)[a]	0.0162(43)	0.8819(40)	0.4890(32)
O(16)[a]	0.5951(46)	0.4558(29)	0.5022(31)
C(1)	0.1471(18)	0.0454(18)	0.1736(19)
C(2)	0.1108(22)	−0.0900(22)	0.1660(23)
C(3)	0.2247(19)	−0.1220(18)	0.2132(20)
C(4)	0.1829(21)	−0.2572(21)	0.1899(22)
C(5)	0.4675(17)	0.5145(17)	0.1714(17)
C(6)	0.6066(19)	0.6281(19)	0.1634(20)
C(7)	0.6410(19)	0.7368(19)	0.2338(20)
C(8)	0.7682(22)	0.8536(22)	0.2021(23)
C(9)	−0.0002(16)	0.3583(16)	0.1828(17)
C(10)	−0.1042(18)	0.3922(18)	0.1812(19)
C(11)	−0.2260(18)	0.2747(18)	0.2310(19)
C(12)	−0.3360(20)	0.3141(19)	0.2013(21)

[a] These atoms have an occupancy factor of 0.5.

TABLE 111b. Thermal Parameters ($\times 10^2$). Anisotropic thermal factors are in the form: $\exp[-2\pi^2(\Sigma U_{ij}h_ih_ja_i^*a_j^*)]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
U	2.2	2.7	6.5	−0.8	0.8	0.8
O(1)	1.2	10.1	8.7	−4.6	−0.4	2.1
O(2)	9.5	5.9	3.0	1.2	0.2	5.4
O(3)	2.7	3.1	13.2	−1.4	2.5	0.8
O(4)	2.0	2.6	9.8	−1.0	1.1	0.3
O(5)	2.3	3.4	9.5	−1.9	0.6	0.9
O(6)	3.0	3.2	10.5	−1.5	1.9	0.7
O(7)	3.0	3.2	9.6	−1.6	1.7	0.5
O(8)	2.9	3.0	10.3	−0.5	2.1	1.1
O(9)	8.7	7.9	7.4	−0.2	2.3	3.4
O(10)	12.8	11.4	9.8	−0.2	3.4	4.6
O(11)	13.6	6.7	12.5	−2.2	4.2	−1.6
N(1)	5.0	4.9	13.7	−3.3	0.4	2.8
N(2)	6.8	4.6	13.9	−2.3	6.1	0.2
N(3)	2.7	6.6	9.0	−1.2	1.7	2.0
N(4)	12.6	4.5	6.5	0.6	2.1	2.1
N(5)	5.4	8.0	7.9	0.7	2.8	3.1
O(12)	12.4	5.2	10.6	−2.3	0.8	4.0
O(13)	12.8	15.6	12.5	4.2	9.7	8.0
O(14)	7.8	16.2	12.0	−3.3	3.4	−3.7
O(15)	14.5	13.2	4.2	0.3	0.3	9.0
O(16)	13.2	4.6	3.8	0.5	1.5	1.6

Atom	*U*	Atom	*U*
C(1)	5.1	C(7)	5.5
C(2)	6.6	C(8)	6.7
C(3)	5.2	C(9)	4.2
C(4)	6.3	C(10)	5.0
C(5)	4.3	C(11)	5.1
C(6)	5.6	C(12)	5.7

TABLE IV. Bond Distances (Å) and Angles (Deg.).

(a) Bond distances	
Coordination	
U–O(1)	1.79(1)
U–O(2)	1.79(1)
U–O(3)	2.45(1)
U–O(4)	2.46(1)
U–O(5)	2.47(1)
U–O(6)	2.46(1)
U–O(7)	2.46(1)
U–O(8)	2.48(1)
Ligands	
C(1)–O(3)	1.24(2)
C(1)–O(4)	1.28(2)
C(1)–C(2)	1.48(3)
C(2)–C(3)	1.48(3)
C(3)–C(4)	1.52(3)
C(4)–N(1)	1.49(3)
C(5)–O(5)	1.25(2)
C(5)–O(6)	1.27(2)
C(5)–C(6)	1.53(2)
C(6)–C(7)	1.52(3)
C(7)–C(8)	1.51(3)
C(8)–N(2)	1.48(3)
C(9)–O(7)	1.29(2)
C(9)–O(8)	1.24(2)
C(9)–C(10)	1.49(2)
C(10)–C(11)	1.53(2)
C(11)–C(12)	1.52(3)
C(12)–N(3)	1.50(2)
Nitrates	
N(4)–O(9)	1.21(2)

(continued on facing page)

TABLE IV. *(continued)*

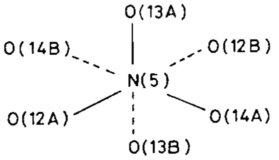
N(4)–O(10)	1.24(3)
N(4)–O(11)	1.20(3)
N(5)–O(12)	1.19(4)
N(5)–O(13)	1.17(8)
N(5)–O(14)	1.20(4)

(b) Bond angles (e.s.d.s are referred to the last significant digit).

Coordination	
O(1)–U–O(2)	177.9(7)
O(3)–U–O(4)	52.0(4)
O(5)–U–O(6)	52.6(4)
O(7)–U–O(8)	52.1(4)
O(3)–U–O(8)	68.3(4)
O(4)–U–O(5)	68.0(3)
O(6)–U–O(7)	67.1(4)
Ligands	
U–O(3)–C(1)	96(1)
U–O(4)–C(1)	95(1)
U–O(5)–C(5)	93(1)
U–O(6)–C(5)	93(1)
U–O(7)–C(9)	95(1)
U–O(8)–C(9)	95(1)
O(3)–C(1)–O(4)	117(2)
O(5)–C(5)–O(6)	121(2)
O(7)–C(9)–O(8)	118(2)
O(3)–C(1)–C(2)	120(2)
O(4)–C(1)–C(2)	122(2)
C(1)–C(2)–C(3)	114(2)
C(2)–C(3)–C(4)	111(2)
C(3)–C(4)–N(1)	112(2)
O(5)–C(5)–C(6)	120(2)
O(6)–C(5)–C(6)	119(2)
C(5)–C(6)–C(7)	113(2)
C(6)–C(7)–C(8)	109(2)
C(7)–C(8)–N(2)	112(2)
O(7)–C(9)–C(10)	120(2)
O(8)–C(9)–C(10)	123(2)
C(9)–C(10)–C(11)	114(2)
C(10)–C(11)–C(12)	110(2)
C(11)–C(12)–N(3)	110(2)
Nitrates	
O(9)–N(4)–O(10)	120(2)
O(9)–N(4)–O(11)	122(2)
O(10)–N(4)–O(11)	118(3)
O(12)–N(5)–O(13)	131(3)
O(12)–N(5)–O(14)	113(4)
O(13)–N(5)–O(14)	111(4)

orthogonal space, indicating a slightly puckered structure. The uranyl distances of 1.79(1) Å are normal and the U–O(ligand) distances (2.45 ÷ 2.48 Å) are in the range expected for compounds where six oxygen atoms (partially charged) are equatorially bonded to uranium. Even if the estimated errors of 0.02 Å do not allow to draw a definite conclusion, the values found show a systematic difference of *ca.* 0.04 Å for the C–O bonds in the three independent carboxylato groups, which could indicate that the negative charge is not equally distributed over the two oxygen atoms.

The situation of the two nitrates is different from a crystallographic point of view. Whereas the $N(4)O_3^-$ ion occupies a general position of the cell, the structure of the second nitrate is complicated by the circumstance that the nitrogen atom N(5) lies on a special position, that is, on the inversion centers of the triclinic cell and, therefore, the oxygen atoms O(12), O(13), and O(14) are statistically distributed over two centrosymmetric positions (A and B) as shown in the Scheme. The refinement of this group was, therefore, carried out assigning an occupancy factor of 0.5 to all these atoms



The water molecule is also interspersed in the cell in a disordered manner and therefore the water oxygen atom was also refined in two positions, with an occupancy factor of 0.5. As shown by the contacts scheme of Table V, the structure is characterized by

TABLE V. Hydrogen Bonds (estimated errors less than 0.03 Å).

N(1)···O(6)^{i}	3.01
N(1)···O(7)^{i}	2.87
N(1)···O(9)^{i}	3.01
N(1)···O(10)^{i}	2.97
N(1)···O(14)	3.02
N(1)···O(12)^{ii}	3.25
N(1)···O(16)^{iii}	3.18
N(2)···O(3)^{iv}	2.96
N(2)···O(8)^{iv}	2.97
N(2)···O(9)	3.02
N(2)···O(15)^{v}	3.04
N(2)···O(15)^{vi}	3.13
N(3)···O(4)^{vii}	2.92
N(3)···O(9)^{vii}	3.14
N(3)···O(10)^{viii}	2.90
N(3)···O(5)^{vii}	3.03
N(3)···O(12)^{vii}	2.97
N(3)···O(13)^{ix}	2.92

Symmetry code:

none	= x, y, z	*v*	= $-1 + x, y, z$
i	= $x, 1 + y, z$	*vi*	= $1 - x, 2 - y, 1 - z$
ii	= $1 - x, -y, -z$	*vii*	= $1 + x, y, z$
iii	= $1 - x, -y, 1 - z$	*viii*	= $-x, 1 - y, 1 - z$
iv	= $-1 + x, -1 + y, z$	*ix*	= $-x, -y, -z$

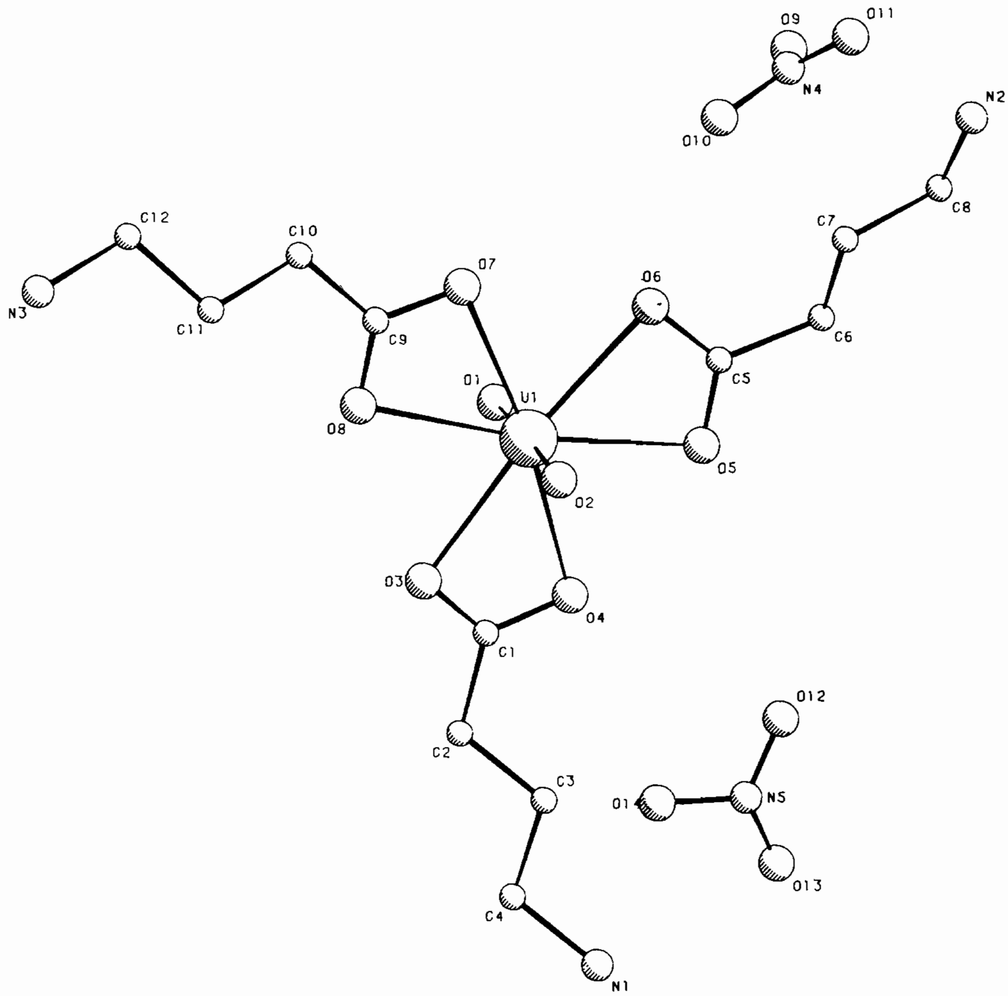


Fig. 2. Molecular structure of $[UO_2(\gamma\text{-aminobutanoic acid})_3](NO_3)_2 \cdot H_2O$. The disordered water molecule is not reported for clarity.

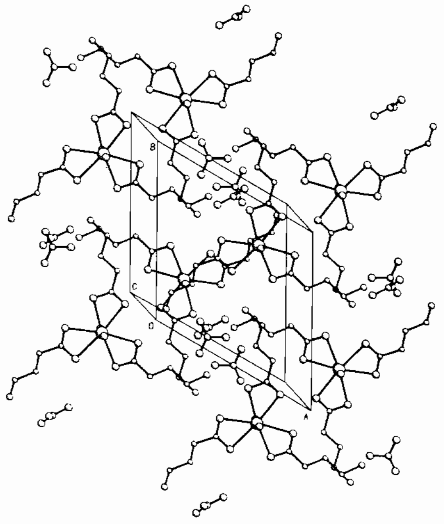


Fig. 3. Molecular packing of $[UO_2(\gamma\text{-aminobutanoic acid})_3](NO_3)_2 \cdot H_2O$. The disordered water molecule is not reported for clarity.

the presence of a complex network of hydrogen bonds from the amino terminals to the carboxylato, nitrate, and water oxygen atoms.

On the basis of the structural determination, the bands at 3140 and 1640 cm^{-1} can be attributed to the protonated amino terminus and the bands at 1530 and 1455 cm^{-1} to the asymmetric and symmetric stretching of the carboxylato group. Because the IR spectra in this region are quite similar, the same zwitterionic form for the aminoacid can be reasonably assumed for all the compounds considered and, therefore, the carboxylato groups must act as bidentate chelating ligands. The presence of a single anion in I and II suggests that the residual charge of the metal must be neutralized by the OH^- group which is not in contradiction with the behaviour of the aminoacids in solution.

Acknowledgement

We thank Mr. L. Rizzo for his technical assistance.

References

1 A. Bismondo, L. Rizzo, G. Tomat, D. Curto, P. Di Bernardo and A. Cassol, *Inorg. Chim. Acta, 74,* 21 (1983); A. Bismondo, U. Casellato, E. Forsellini and R. Graziani, *J. Crystallogr., Spectrosc. Res., 15,* 257 (1985).

2 A. Bismondo, work in progress.

3 L. Magon, R. Portanova, B. Zarli and A. Bismondo, *J. Inorg. Nucl. Chem., 34,* 1971 (1972).

4 L. J. Bellamy, 'The Infrared Spectra of Complex Molecules', Methuen, London (1966).

5 A. C. T. North, D. C. Phillips and F. S. Mathews, *Acta Crystallogr., Sect. A:, 24,* 351 (1968).

6 G. Sheldrick, 'SHELX', System of Crystallographic Programs, Univ. of Cambridge, 1976.

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