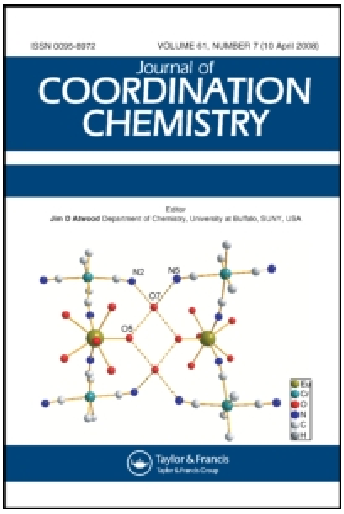

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Synthesis and Crystal Structure of $[(C1A1(\mu\text{-}OH)_2A1C1)\cdot 18\text{-Crown-}6][AIC1_4]_2\cdot 8/3\ C_6H_5NO_2$, a Complex Featuring a Binuclear Aluminum-Containing Cation Threaded Through 18-Crown-6

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SYNTHESIS AND CRYSTAL STRUCTURE OF $[(ClAl(\mu\text{-}OH)_2AlCl)\cdot 18\text{-}CROWN\text{-}6][AlCl_4]_2\cdot 8/3C_6H_5NO_2$, A COMPLEX FEATURING A BINUCLEAR ALUMINUM-CONTAINING CATION THREADED THROUGH 18-CROWN-6

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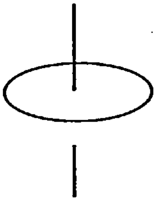
(Received November 19, 1990)

The title compound resulted from the partial hydrolysis of the reaction product of $AlCl_3$, 18-crown-6, and HCl(g) in nitrobenzene. The compound crystallizes in the triclinic space group $P\bar{1}$ with $a = 13.344(2)$, $b = 17.742(3)$, $c = 18.318(3)$Å, $\alpha = 68.69(1)$, $\beta = 81.98(1)$, $\gamma = 68.00(1)°$, and $D_c = 1.45\ \mathrm{g\,cm^{-3}}$ for $Z = 3$. In the crystal structure the 2+ binuclear aluminum-containing cation is threaded through the crown ether with each aluminum atom coordinated to three crown ether oxygen atoms. The crystal is composed of alternating layers of cations, layers of anions, and bilayers of nitrobenzene molecules.

Keywords: Aluminum, crown ether, crystal structure, threaded complex

INTRODUCTION

Crown ethers now play an important role in many areas of chemistry. Particularly valuable contributions on the complexation of metal ions have been realized.[1,2] With regard to main group metals, multidentate coordination by crown ethers results in a situation in which the metal and associated ligands are either threaded through[3-8] (**1**) or perching on[9] (**2**) the crown ether. Until now binuclear main group metal complexes have been restricted to those of Na^+ [10] and K^+,[11] although Martell and co-workers have developed a rich chemistry of binuclear transition metal complexes with a variety of macrocycles.[12-15] We report here a complex in which a binuclear aluminum species is threaded through an 18-crown-6 molecule.



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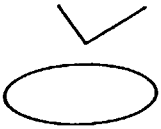

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EXPERIMENTAL

Synthesis of $[(ClAl(\mu\text{-}OH)_2AlCl)\cdot 18\text{-crown-}6][AlCl_4]_2\cdot 8/3C_6H_5NO_2$

All substances were reagent grade chemicals. The reaction was carried out on t bench top and a cover gas was not used. Aluminum trichloride (0.33 g, 2.5 mm was dissolved in 10 cm^3 of nitrobenzene in a tube fitted with a screw top. 18-Crown (0.66 g, 2.5 mmol) was added to the solution with stirring. Gaseous HCl was th bubbled through the solution for 15 min. The vessel was allowed to cool and sin crystals formed over the two-day period. The hydrolysis occurred from the wat which the HCl(g) carried into the solution.

X-ray Structure Determination

Single crystals were mounted in thin-walled glass capillaries with a drop of moth liquor. Final lattice parameters as determined from the least-squares refinement the angular settings for 25 reflections (2θ > 30°) are given in Table I. Data we collected on an Enraf-Nonius CAD4 diffractometer using the θ-2θ scan techniq as described previously.[16] A summary of data collection and structure soluti parameters is also given in Table I. The intensities were corrected f Lorentz, polarization and absorption effects. The latter was accomplished by the scan method. Calculations were carried out using the SHELX system of compu programs.[17]

TABLE I

Summary of crystallographic data.

Mol. wt.	1087
Space group	$P\bar{1}$
Cell constants	
a, Å	13.344(2)
b, Å	17.741(3)
c, Å	18.318(3)
α, deg	68.69(1)
β, deg	81.98(1)
γ, deg	68.00(1)
Cell vol., Å^3	3746
Molecules/unit cell	3
D_c(calcd), g cm^{-3}	1.45
Radiation	MoKα
Max. crystal dimensions., mm	0.34 × 0.45 × 0.62
Scan width, deg.	0.80 + 0.35 tan θ
Std. reflections	900, 0110, 0012
Decay of standards	<2%
Reflections measured	14 817
2θ range, deg.	2–50
Observed reflections	3061
No. of parameters varied	390
R	0.094
R_w	0.099

TABLE II
Final fractional coordinates and isotropic temperature factors.

Atom	*x*/*a*	*y*/*b*	*z*/*c*	*U*(eqv)
Al(1)	−.0684(6)	.3412(4)	−.0154(4)	0.035(1)
Al(2)	−.2743(7)	.3221(5)	.0333(4)	0.052(12)
Al(3)	.6024(8)	.0087(5)	.9753(5)	0.073(16)
Al(4)	.3241(8)	.2346(5)	.2723(4)	0.066(37)
Al(5)	.3348(7)	.4104(5)	.7388(5)	0.070(11)
Al(6)	−.005(1)	.1044(7)	.7402(6)	0.112(5)
Cl(1)	.0847(6)	.3167(4)	.0472(4)	0.068(28)
Cl(2)	−.4155(5)	.3391(4)	−.0259(4)	0.056(15)
Cl(3)	.7521(5)	−.0145(4)	1.0312(5)	0.070(45)
Cl(4)	.3462(6)	.2818(4)	.1456(3)	0.059(22)
Cl(5)	.1867(7)	.3322(4)	.2980(4)	0.078(28)
Cl(6)	.4659(5)	.2207(4)	.3233(3)	0.068(18)
Cl(7)	.2951(6)	.1197(3)	.3025(3)	0.070(36)
Cl(8)	.3131(8)	.3821(5)	.8618(5)	0.101(37)
Cl(9)	.490(2)	.308(1)	.705(1)	0.157(8)
Cl(10)	.306(1)	.3131(9)	.7199(8)	0.082(4)
Cl(11)	.227(2)	.405(1)	.676(1)	0.156(8)
Cl(12)	.188(2)	.543(1)	.698(1)	0.131(7)
Cl(13)	.364(2)	.527(2)	.684(2)	0.059(8)
Cl(14)	.0292(6)	.0621(4)	.8622(4)	0.076(2)
Cl(15)	.146(1)	.1693(8)	.6746(7)	0.070(3)
Cl(16)	.125(1)	.0308(9)	.6975(8)	0.069(3)
Cl(17)	.135(2)	.082(1)	.705(1)	0.120(6)
Cl(18)	.034(2)	.239(2)	.708(2)	0.049(8)
O(1)	−.1187(9)	.4645(7)	−.0349(6)	0.023(3)
O(4)	−.008(1)	.3774(8)	−.1163(7)	0.043(3)
O(7)	−.001(1)	.2286(9)	−.0337(8)	0.046(4)
O(10)	−.216(1)	.2017(8)	.0505(7)	0.042(3)
O(13)	−.318(1)	.2847(9)	.1416(8)	0.047(4)
O(16)	−.339(1)	.4340(9)	.0462(8)	0.052(4)
O(100)	−.1944(9)	.3566(7)	−.0557(6)	0.024(3)
O(101)	−.135(1)	.3103(8)	.0751(7)	0.042(3)
O(21)	.664(1)	−.100(1)	.959(1)	0.086(5)
O(24)	.649(2)	.052(1)	.870(1)	0.094(6)
O(27)	.553(2)	.137(1)	.961(1)	0.105(7)
O(201)	.474(2)	.023(1)	.940(1)	0.105(6)
C(2)	−.099(1)	.516(1)	−.114(1)	0.029(4)
C(3)	.003(2)	.464(1)	−.139(1)	0.030(4)
C(5)	.076(2)	.305(1)	−.135(1)	0.037(5)
C(6)	.045(1)	.236(1)	−.111(1)	0.027(4)
C(8)	−.031(2)	.150(1)	.014(1)	0.027(4)
C(9)	−.138(1)	.1529(9)	.0014(9)	0.011(3)
C(11)	−.217(2)	.153(1)	.132(1)	0.033(5)
C(12)	−.318(2)	.197(1)	.167(1)	0.034(5)
C(14)	−.406(2)	.348(2)	.167(2)	0.086(9)
C(15)	−.370(2)	.432(1)	.127(1)	0.035(5)
C(17)	−.323(3)	.514(2)	−.006(2)	0.104(10)
C(18)	−.194(2)	.509(2)	.015(2)	0.092(9)
C(22)	.663(3)	−.079(2)	.867(2)	0.127(12)
C(23)	.731(2)	−.013(1)	.840(1)	0.061(7)

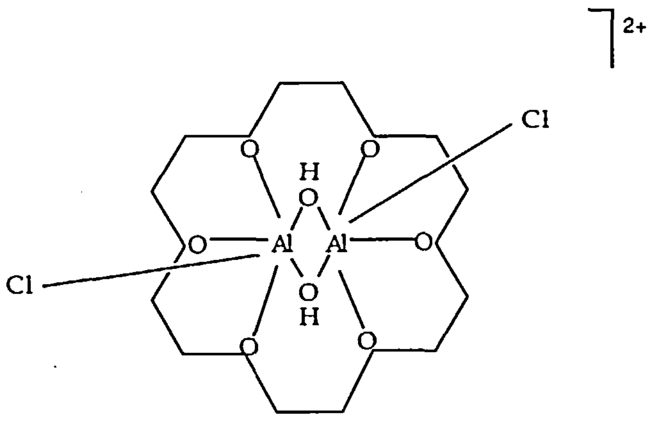
TABLE II

Atom	*x*/*a*	*y*/*b*	*z*/*c*	*U*(eqv)
C(25)	.681(4)	.132(3)	.850(3)	0.223(22)
C(26)	.577(3)	.194(3)	.890(2)	0.160(15)
C(28)	.456(2)	.168(2)	1.008(1)	0.074(8)
C(29)	.643(2)	−.175(1)	.997(1)	0.051(6)
O(300)	.577(1)	.091(1)	.221(1)	0.082(5)
O(301)	.572(1)	.036(1)	.215(1)	0.086(5)
N(301)	.582(2)	−.042(2)	.253(2)	0.111(8)
C(301)	.614(2)	−.071(2)	.336(2)	0.071(7)
C(302)	.596(2)	−.017(2)	.376(2)	0.080(8)
C(303)	.636(3)	−.053(2)	.464(2)	0.124(11)
C(304)	.684(2)	−.146(2)	.491(2)	0.086(8)
C(305)	.688(3)	−.189(2)	.457(2)	0.132(13)
C(306)	.644(3)	−.155(3)	.370(2)	0.149(14)
O(401)	.747(2)	.395(2)	.782(1)	0.129(8)
O(402)	.657(2)	.514(1)	.780(1)	0.121(8)
N(401)	.699(3)	.475(2)	.750(2)	0.160(13)
C(401)	.692(3)	.488(2)	.670(2)	0.115(11)
C(402)	.636(2)	.571(2)	.626(2)	0.098(9)
C(403)	.628(3)	.584(2)	.553(2)	0.134(13)
C(404)	.645(3)	.541(2)	.511(2)	0.124(12)
C(405)	.694(2)	.454(2)	.548(2)	0.099(9)
C(406)	.721(3)	.422(2)	.628(2)	0.131(12)
C(501)	.937(2)	.282(3)	.217(1)	0.178(7)
C(502)	.910(2)	.333(3)	.265(1)	0.178(7)
C(503)	.935(2)	.294(3)	.344(1)	0.178(7)
C(504)	.987(2)	.205(3)	.376(1)	0.178(7)
C(505)	1.014(2)	.154(3)	.328(1)	0.178(7)
C(506)	.989(2)	.193(3)	.249(1)	0.178(7)
C(601)	−.300(3)	.204(3)	.432(1)	0.207(8)
C(602)	−.343(3)	.264(3)	.471(1)	0.207(8)
C(603)	−.371(3)	.236(3)	.550(1)	0.207(8)
C(604)	−.356(3)	.149(3)	.590(1)	0.207(8)
C(605)	−.313(3)	.090(3)	.551(1)	0.207(8)
C(606)	−.285(3)	.117(3)	.472(1)	0.207(8)
N(601)	−.285(3)	.228(2)	.353(2)	0.096(9)
O(601)	−.253(3)	.188(2)	.315(2)	0.076(10)
O(602)	−.312(3)	.295(3)	.318(2)	0.101(12)

Structure solution was effected by application of direct methods and difference Fourier techniques. Several crystals were used, but none scattered well. This difficulty is readily explained in terms of the final structure, but structure solution was a lengthy process. Only one of the $[AlCl_4]^-$ anions was well defined. The others suffered from disorder. Two of the nitrobenzene molecules were constructed using idealized geometry and were refined as rigid groups. Because of the paucity of diffraction data, only the full occupancy aluminum and chlorine atoms were refined with anisotropic thermal parameters. Hydrogen atoms were placed in calculated positions and were not refined. The final *R* value was 0.094 based on 3061 observed reflections. The weighting scheme was based on unit weights. The final values of the positional parameters are given in Table II. Tables of anisotropic thermal parameters, hydrogen atom coordinates and structure factors are available from J.L.A.

RESULTS AND DISCUSSION

A schematic representation of the 2+ binuclear aluminum-containing cation is given in 3, and the structure of one of the two crystallographically independent cations is displayed as Figure 1. Each aluminum atom exhibits octahedral coordination with three crown ether oxygen atoms arranged in a meridional fashion. The cation shown in the Figure resides on a crystallographic centre of inversion. The aluminum atom shows significant angular deviations from those of exact octahedral symmetry, as expected with a terdentate ligand and bridging groups. The Al–O(crown) distances, 1.90(2), 1.91(2), and 2.04(2) Å are reasonable compared to those found in related complexes,[3,5,9,18,19] as are the Al–O(hydroxyl) lengths of 1.76(1) and 1.80(1) Å.[20] The Al–Cl distance of 2.20(1) Å is also in the normal range.[3,9] However, in the other independent cation quite significant deviations (Table III) are found. For example, the Al(1)–Cl(1) distance is 2.30(1) Å, while that for Al(2)–Cl(2) is 2.17(1) Å. Although the collection and refinement of the data suffered from difficulties (as described in Experimental), it is likely that the distortions are real, possibly connected to the packing of the cations and anions in the layered structure.



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The conformation of the two crown moieties is essentially the same. The oxygen atoms of the one containing Al(1) and Al(2) are planar to within 0.47 Å with Al(1) 0.52 Å above the plane and Al(2) 0.59 Å below it. Similarly, Al(3) lies 0.54 Å above and Al(3)′ lies 0.54 Å below the plane of the oxygen atoms of the second crown (which is planar to within 0.43 Å). The plane of the hydroxyl oxygen atoms and aluminum atoms is normal to the plane of the crown ether oxygen atoms. The cation may be viewed as comprising $[(ClAl(\mu\text{-}OH)_2AlCl)]^{2+}$ threaded through the crown ether.

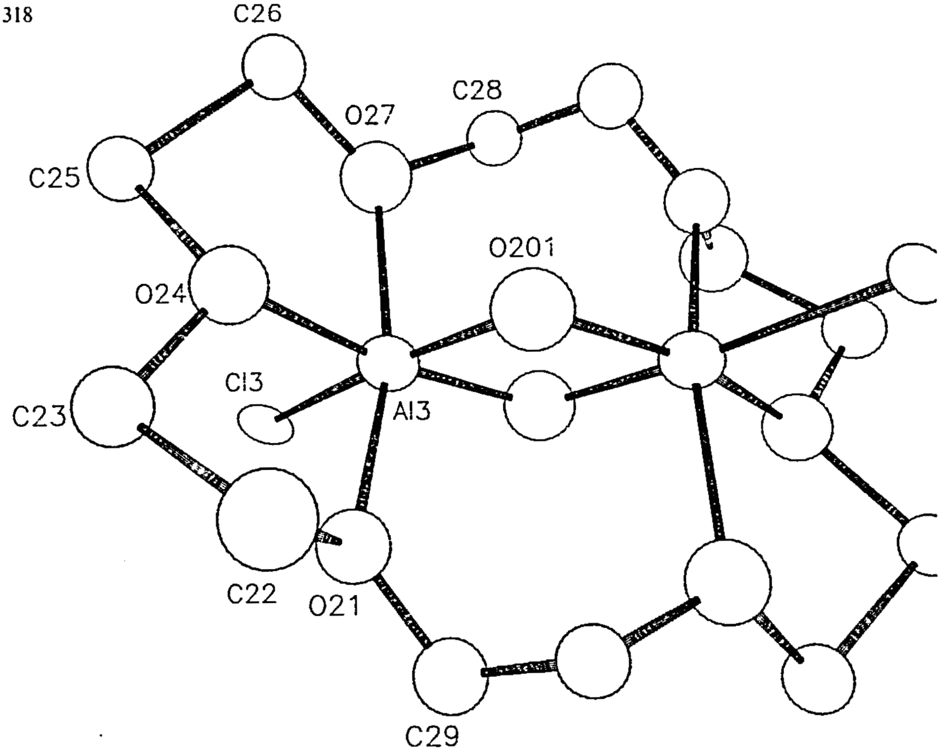

FIGURE 1 One of the two crystallographically independent $[(ClAl(\mu\text{-}OH)_2AlCl)\cdot 18\text{-crown-}6]^{2+}$ cations.

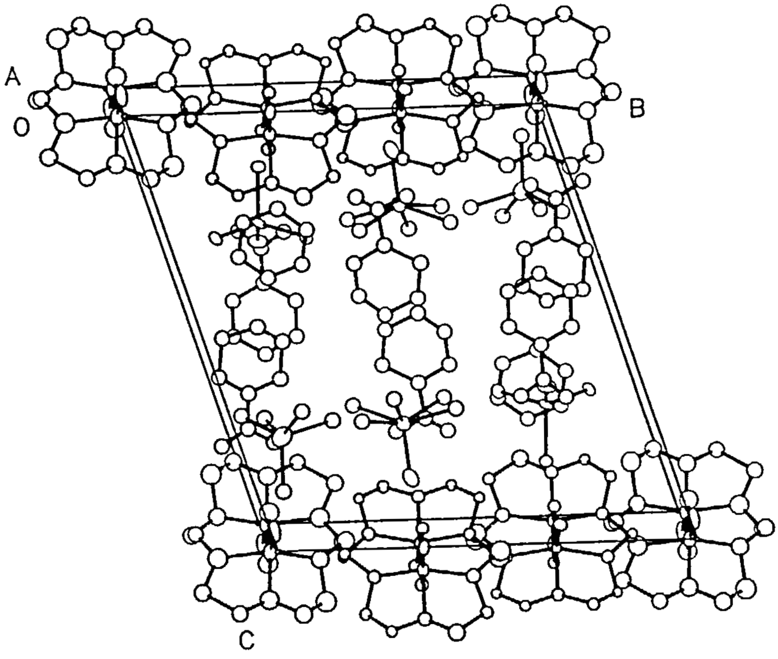

FIGURE 2 Unit cell packing showing the layer structure of the crystal.

TABLE III
Selected bond distances (Å) and angles (degrees) involving the cation.

Atoms	Distance	Atoms	Distance
Al(1)-Cl(1)	2.30(1)	Al(1)-O(1)	1.94(1)
Al(1)-O(4)	1.89(1)	Al(1)-O(7)	1.99(1)
Al(1)-O(100)	1.82(1)	Al(1)-O(101)	1.77(1)
Al(2)-Cl(2)	2.17(1)	Al(2)-O(10)	1.90(1)
Al(2)-O(13)	1.93(2)	Al(2)-O(16)	1.93(2)
Al(2)-O(100)	1.86(1)	Al(2)-O(101)	2.01(2)
Al(3)-Cl(3)	2.20(1)	Al(3)-O(21)	1.91(2)
Al(3)-O(24)	1.90(2)	Al(3)-O(27)	2.04(2)
Al(3)-O(201)	1.80(2)	Al(3)-O(201)′	1.76(1)

Atoms	Angle	Atoms	Angle
Cl(1)-Al(1)-O(1)	92.5(5)	Cl(1)-Al(1)-O(4)	93.2(5)
O(1)-Al(1)-O(4)	80.5(6)	Cl(1)-Al(1)-O(7)	91.1(5)
O(1)-Al(1)-O(7)	160.1(6)	O(4)-Al(1)-O(7)	79.8(6)
Cl(1)-Al(1)-O(100)	174.6(5)	O(1)-Al(1)-O(100)	88.8(6)
O(4)-Al(1)-O(100)	92.2(6)	O(7)-Al(1)-O(100)	89.5(6)
Cl(1)-Al(1)-O(101)	91.7(5)	O(1)-Al(1)-O(101)	98.5(6)
O(4)-Al(1)-O(101)	175.0(8)	O(7)-Al(1)-O(101)	100.9(6)
O(100)-Al(1)-O(101)	82.9(7)	Cl(2)-Al(2)-O(10)	92.7(6)
Cl(2)-Al(2)-(O13)	101.0(6)	O(10)-Al(2)-O(13)	83.2(6)
Cl(2)-Al(2)-O(16)	93.0(6)	O(10)-Al(2)-O(16)	164.5(7)
O(13)-Al(2)-O(16)	81.5(6)	Cl(2)-Al(2)-O(100)	97.4(5)
O(10)-Al(2)-O(100)	97.4(6)	O(13)-Al(2)-O(100)	161.5(8)
O(16)-Al(2)-O(100)	96.1(6)	Cl(2)-Al(2)-O(101)	173.0(6)
O(10)-Al(2)-O(101)	87.9(7)	O(13)-Al(2)-O(101)	85.9(6)
O(16)-Al(2)-O(101)	88.2(7)	O(100)-Al(2)-O(101)	75.6(6)
Cl(3)-Al(3)-O(21)	91.1(7)	Cl(3)-Al(3)-O(24)	96.1(7)
O(21)-Al(3)-O(24)	83.0(9)	Cl(3)-Al(3)-O(27)	89.9(7)
O(21)-Al(3)-O(27)	163.3(9)	O(24)-Al(3)-O(27)	80.3(9)
Cl(3)-Al(3)-O(201)	173.6(9)	O(21)-Al(3)-O(201)	89.6(9)
O(24)-Al(3)-O(201)	90(1)	O(27)-Al(3)-O(201)	91.3(9)
Cl(3)-Al(3)-O(201)′	100(1)	O(21)-Al(3)-O(201)′	98(1)
O(24)-Al(3)-O(201)′	164(1)	O(27)-Al(3)-O(201)′	99(1)
O(201)′-Al(3)-O(201)	74(1)		

The unit cell packing is illustrated in Figure 2. It is clearly seen that the crystal is made up of layers of cations, layers of anions, bilayers of nitrobenzene molecules, layers of anions, layers of cations, and so forth. Two full occupancy solvent molecules and one of 2/3 occupancy have been located; however, this layer is still ill-defined. The portions of the anions which are packed closest to the solvent molecules also suffer from rotational disorder.

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REFERENCES

1. C.J. Pedersen, *J. Incl. Phenom.*, **6**, 337 (1988).
2. Y. Inoue and G.W. Gokel, "Cation Binding by Macrocycles," (Dekker, New York, 1990).
3. S.G. Bott, H. Elgamal and J.L. Atwood, *J. Am. Chem. Soc.*, **107**, 1796 (1985).
4. H.G. Richey, Jr. and D.M. Kushlan, *J. Am. Chem. Soc.*, **109**, 2510 (1987).
5. S.G. Bott, A. Alvanipour, S.D. Morley, D.A. Atwood, C.M. Means, A.W. Coleman and J. Atwood. *Angew. Chem., Int. Ed. Engl.*, **26**, 485 (1987).
6. A.D. Pajerski, M. Parvez and H.G. Richey, Jr., *J. Am. Chem. Soc.*, **110**, 2660 (1988).
7. A.D. Pajerski, G.L. BersStresser, M. Parvez and H.G. Richey, Jr., *J. Am. Chem. Soc.*, **110**, 48 (1988).
8. P.R. Marlies, T. Nomoto, O.S. Akkerman, F. Bickelhaupt, W.J.J. Smeets and A.L. Spek, *J. A Chem. Soc.*, **110**, 4845, (1988).
9. J.L. Atwood, H. Elgamal, G.H. Robinson, S.G. Bott, J.A. Weeks and W.E. Hunter, *J. Incl. Phenor* **2**, 367 (1984).
10. D.L. Hughes, *J. Chem. Soc., Dalton Trans.*, 2374 (1975).
11. D.E. Fenton, M. Mercer, N.S. Poonia and M.R. Truter, *J. Chem. Soc., Chem. Comm.*, 66 (1972
12. R.J. Motekaitis, P.R. Rudolf, A.E. Martell and A. Clearfield, *Inorg. Chem.*, **28**, 112 (1989).
13. M.G. Basallote, D. Chen and A.E. Martell, *Inorg. Chem.*, **28**, 3494 (1989), and references thereir
14. R. Menif, D. Chen and A.E. Martell, *Inorg. Chem.*, **28**, 4633 (1989).
15. B. Szpoganicz, R.J. Motekaitis and A.E. Martell, *Inorg. Chem.*, **29**, 1467 (1990), and referenc therein.
16. J. Holton, M.F. Lappert, D.G.H. Ballard, R. Pearce, J.L. Atwood and W.E. Hunter, *J. Chem. So Dalton Trans.*, 45 (1979).
17. SHELX, a system of computer programs for X-ray structure determination by G.M. Sheldri (1976).
18. M.B. Power, A.W. Apblett, S.G. Bott, J.L. Atwood and A.R. Barron, *Organometallics*, **9**, 25 (1990).
19. A.W. Apblett and A.R. Barron, *Organometallics*, **9**, 2137 (1990).
20. J.L. Atwood, C. Jones, C.L. Raston, S.G. Bott and G.W. Orr, unpublished results.