Acta Chemica Scandinavica A 38 (1984) 801–806

The Crystal Structure of Ammonium Fluoro-oxodiperoxovanadate(2–), $(NH_4)_2[VFO(O_2)_2]$

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The crystal structure of $(NH_4)_2[VFO(O_2)_2]$ has been determined and refined from single-crystal X-ray diffractometer data to a final R_F-value of 0.035 for 2301 observed reflexions. The compound crystallizes in the monoclinic space group $P2_1/c$ (No. 14) with a=6.123(2), b=11.319(4), c=8.076(2) Å, β=89.95(3)° and Z=4.

Each vanadium atom is seven-coordinated in the pentagonal-bipyramidal way. The two peroxo groups and the fluorine atom form the equatorial plane and the double-bonded oxygen atom in one $VFO(O_2)_2^{2-}$ unit occupies the apical position in that unit as well as the second apical position in the neighbouring unit. The anions can be described as zigzag chains, extending along the crystallographic c-direction, of pentagonal bipyramids sharing the apical corners, the V=O···V angle being 157.1(1)°. Most of the crystals obtained were twins and the twin formation is discussed.

Bond distances: $V{=}O_{apical}$ 1.613(1) Å, $V{-}O_{apical}$ 2.505(1) Å, V–F 1.929(1) Å, *trans* $V{-}O_{peroxo}$ 1.905(1) and 1.903(1) Å, *cis* $V{-}O_{peroxo}$ 1.874(2) and 1.880(2) Å, $(O{-}O)_{peroxo}$ 1.460(2) and 1.462(2) Å, and N–H 0.75(5)–0.89(4) Å.

In the system $NH_4^+-V_2O_5-F^--H_2O_2$ the present authors have isolated and characterized two different compounds hitherto, *i.e.* $(NH_4)_2[VFO(O_2)_2]$ and $(NH_4)_3[VF_2O(O_2)_2]$.[1] Further species have been synthetized and studied spectroscopically by Schwendt *et al.*[2] On prolonged standing in contact with the mother liquor, the orange-yellow, band-shaped crystals of $(NH_4)_2[VFO(O_2)_2]$ are often transformed into polycrystalline aggregates of yellow, prismatic crystals of $(NH_4)_3[VF_2O(O_2)_2]$. In the corresponding potassium system the remarkably stable yellow, plate-formed crystals of $K_2[VFO(O_2)_2]$ do not appear to be converted.[3] Despite the same stoichiometry and almost the same cell dimensions, $(NH_4)_2[VFO(O_2)_2]$ and $K_2[VFO(O_2)_2]$ are not isomorphous,[3] but crystallize in different space groups, $K_2[VFO(O_2)_2]$ in $P2_12_12_1$ and $(NH_4)_2[VFO(O_2)_2]$ in $P2_1/c$. Because of these apparent differences between $K_2[VFO(O_2)_2]$ and $(NH_4)_2[VFO(O_2)_2]$ a structure analysis of the latter, was considered advantageous.

EXPERIMENTAL

Preparation. A mixture of 0.46 g vanadium(V) oxide and 1.8 g ammonium fluoride was dissolved in 15 ml 15 % hydrogen peroxide. Band-shaped, orange-yellow crystals were developed within two days at room temperature. All these crystals were somewhat striated, and were shown during the structure analysis to be twins. Later on, when the structure had been solved, an alternate preparative method was used, similar to the one described by Schwendt *et al.*[2] 0.60 g ammonium *meta*-vanadate was dissolved in 10 ml 12 % hydrogen peroxide and 2.2 g ammonium fluoride was added. The solution was kept at +4 °C. After 5 days crystals of the same appearance as above were developed. From a non-striated region in one crystal a fragment was cut out; this turned out to be a single crystal and was used to refine the structure. The peroxide content was checked by permanganate titration and vanadium was determined gravimetrically as $AgVO_3$ (Found: O_2^{2-} 34.2; V 27.4. Calc. for $(NH_4)_2[VFO(O_2)_2]$: O_2^{2-} 34.40; V 27.39).

0302-4377/84 $2.50

X-Ray methods. X-Ray powder photographs were obtained by the Guinier-Hägg method (Cu$K\alpha$ radiation). Approximate cell dimensions and the space group were derived from single-crystal X-ray photographs taken with a Weissenberg camera (Cu$K\alpha$ radiation). Intensity data were recorded at 18 °C using a SYNTEX $P2_1$ automatic four-circle single-crystal X-ray diffractometer, graphite-monochromatized Mo$K\alpha$ radiation and three different crystals, two of which were shown during the structure analysis to be twins. From the first of these the structure was solved, but refinement was deferred until data for a third crystal, which proved to be a single crystal, were obtained. This had the dimensions 0.13×0.15×0.19 mm. The ω-2θ scan method was used and the 2θ scan speed was allowed to vary between 2.5 and 29.3 °min.$^{-1}$ Data were collected for $2\theta \leqq 80.0°$ and were processed as described in Ref. 1. A total of 3633 independent reflexions were measured and 2301, having $I \geqq 3\sigma(I)$, were considered observed. The unit cell parameters were determined from a least-squares fit of refined diffractometer setting angles for 15 reflexions.

CRYSTAL DATA

$(NH_4)_2[VFO(O_2)_2]$, F.W.=186.01.
Space group $P2_1/c$ (No. 14).
a=6.123(2) Å, b=11.319(4) Å, c=8.076(2) Å, β=89.95(3)°, V=559.7(3) Å^3, Z=4, D_o=2.22 g cm^{-3}, D_c=2.207 g cm^{-3}, μ(Mo$K\alpha$)=1.70 mm^{-1}.

STRUCTURE DETERMINATION

The structure was solved by Patterson and electron density calculations. The first two crystals studied showed pseudo-orthorhombic symmetry. According to the systematically absent reflexions, $h0l$ for $l=2n+1$ and $0k0$ for $k=2n+1$, and the fact that $I(hkl)$ differed slightly from $I(hk\bar{l})$, the compound crystallizes, however, in the unique monoclinic space group $P2_1/c$. The general heavy-heavy-atom vectors had peak heights of only 60 % (50 %) of those expected, (values in parentheses refer to the second crystal.) On the other hand, there were unexpected peaks with peak heights of 40 % (50 %) of general heavy-heavy-atom peak heights. This indicated disorder or twin formation. Disorder is not uncommon among peroxometallates, examples being $K_2[VFO(O_2)_2]$,[3] $(NH_4)_3[TiF_5(O_2)]$,[4,5] $Na_2[NbF_5(O_2)]\cdot 2H_2O$,[6] $(C_{12}H_{10}N_2)[NbF_5(O_2)]$,[7] and $(C_9H_8NO)_2[NbF_5(O_2)]\cdot 3H_2O$.[8] The possibility of disorder with vanadium in two partly occupied four-fold positions, V1 and V2, with occupation numbers about 0.6 and 0.4 (0.5 and 0.5), could, however, be ruled out since V1–V2 vectors were lacking in the Patterson maps. Due to the striated appearance of the crystals they were more likely to be twins. Despite this a plausible structure was deduced, but, ignoring twinning, it could not be refined below R=0.22 (0.26) ($R=\sum||F_o|-|F_c||/\sum|F_o|$).

The Weissenberg photographs and the peak profiles obtained by the diffractometer showed no splitting of the reflexions, neither were any diffuse reflexions, typical for an OD-structure, observed. Furthermore, each $F_o(hkl)$ was roughly the average of $F_c(hkl)$ and $F_c(hk\bar{l})$. From these observations twin formation with two twin parts, A and B, with antiparallel orientations such that an hkl-reflexion from part A coincides with an $hk\bar{l}$-reflexion from part B would seem likely. Since each reflexion intensity is then the sum of two independent intensities, $I_A(hkl)$ and $I_B(hk\bar{l})$, the observed structure factors should, therefore, be compared with a calculated 'structure factor' $|F_{c,t}(hkl)|=[x_A|F_c(hkl)|^2+(1-x_A)|F_c(hk\bar{l})|^2]^{\frac{1}{2}}$, where x_A is the fraction of twin fragment A. As a consequence of this the Patterson function should be a superposition of two independent Patterson functions, thus explaining the number and magnitudes of the observed peaks. Refinement according to the expression for $F_{c,t}(hkl)$ was not performed since a single crystal was finally obtained. Using the parameters obtained from the twin data for the non-hydrogen atoms, refinement with the new data set reduced the R-value to 0.067 with isotropic and to 0.041 with anisotropic thermal parameters. All hydrogen atoms were located from an electron density difference map. Refinement of positional parameters for all atoms, anisotropic thermal parameters for the non-hydrogen atoms and isotropic ones for the hydrogen atoms, gave a final R-value of 0.035. The idea of the twin formation was further tested by calculating the R-value using the above-mentioned equation for $F_{c,t}(hkl)$; with the final parameters and with x_A=0.6 this R-value became 0.048.

The weights used in the full-matrix refinement were calculated according to $w=(40+|F_o|+0.01|F_o|^2+0.001|F_o|^3)^{-1}$.[9] The scattering factors for V, F, O, N and H were taken

Table 1. Fractional atomic coordinates and equivalent isotropic thermal parameters for $(NH_4)_2[VFO(O_2)_2]$. $U_{eq}=\frac{1}{3}\sum_i\sum_j U_{ij}a_i^*a_j^*a_ia_j\cos\alpha_{ij}$. All atoms occupy the general four-fold site 4*e* of space group $P2_1/c$.

Atom	*x*	*y*	*z*	$U_{eq}/Å^2$ ($U_{iso}/Å^2$ for H)
V	0.20063(4)	0.24363(2)	0.45729(3)	0.0141(1)
F	−0.1094(2)	0.2433(1)	0.4997(2)	0.0266(5)
O1	0.2048(3)	0.0882(1)	0.5475(2)	0.0264(7)
O2	0.4210(3)	0.1414(1)	0.5309(2)	0.0289(7)
O3	0.4058(3)	0.3671(1)	0.4632(2)	0.0284(7)
O4	0.1815(3)	0.4113(1)	0.4658(2)	0.0267(7)
O5	0.1863(3)	0.2151(1)	0.2619(2)	0.0239(6)
N1	−0.3022(3)	0.1130(2)	0.2349(2)	0.0260(7)
N2	−0.2209(3)	0.0571(2)	0.7415(2)	0.0256(7)
H1	−0.273(6)	0.037(4)	0.223(5)	0.023(10)
H2	−0.209(8)	0.153(4)	0.176(6)	0.037(12)
H3	−0.322(7)	0.133(4)	0.321(6)	0.034(11)
H4	−0.406(7)	0.124(4)	0.180(5)	0.027(10)
H5	−0.226(7)	0.009(4)	0.655(5)	0.028(10)
H6	−0.207(6)	0.012(3)	0.826(5)	0.018(9)
H7	−0.331(7)	0.094(4)	0.750(5)	0.024(10)
H8	−0.110(7)	0.103(4)	0.730(5)	0.027(10)

from Ref. 10. An electron density difference map calculated after the final cycle of refinement showed no peak higher than 0.64 e $Å^{-3}$. Calculations were carried out on an IBM 3033 computer using the crystallographic programmes described in Ref. 11. Lists of the structure factors and thermal parameters are available from the authors on request.

RESULTS AND DISCUSSION

Positional parameters and U_{eq} are given in Table 1, distances and angles in Table 2 and hydrogen bond distances in Table 3. Fig. 1 shows the positions of the non-hydrogen atoms in the unit cell and Fig. 2 the coordination about vanadium.

Table 2. Bond distances (Å) and angles (°) in $(NH_4)_2[VFO(O_2)_2]$.

Distance		Angle		Angle	
V–F	1.929(1)	F–V–O1	86.77(7)	O3–V–O4	45.47(7)
V–O1	1.905(1)	F–V–O2	130.61(7)	O3–V–O5	102.12(7)
V–O2	1.874(2)	F–V–O3	130.88(7)	O3–V–O5′	81.95(6)
V–O3	1.880(2)	F–V–O4	86.25(6)	O4–V–O5	103.41(7)
V–O4	1.903(1)	F–V–O5	96.88(7)	O4–V–O5′	77.07(6)
V–O5	1.613(1)	F–V–O5′	77.97(5)	O5–V–O5′	174.81(9)
V–O5′	2.505(1)	O1–V–O2	45.46(7)	V–O1–O2	66.17(9)
O1–O2	1.460(2)	O1–V–O3	131.94(7)	V–O2–O1	68.37(9)
O3–O4	1.462(2)	O1–V–O4	155.30(6)	V–O3–O4	68.11(9)
N1–H1	0.89(4)	O1–V–O5	100.94(7)	V–O4–O3	66.43(8)
N1–H2	0.87(5)	O1–V–O5′	78.30(6)	V–O5–V′	157.10(8)
N1–H3	0.75(5)	O2–V–O3	88.29(8)		
N1–H4	0.78(4)	O2–V–O4	130.45(7)		
N2–H5	0.89(4)	O2–V–O5	103.06(7)		
N2–H6	0.86(4)	O2–V–O5′	80.14(6)		
N2–H7	0.80(4)				
N2–H8	0.86(4)				

Table 3. Cation environment in $(NH_4)_2[VFO(O_2)_2]$. Distances less than 3.2 Å are included.

	Distance/Å		Distance/Å
N1···F^{i}	2.765(2)	N2···O2^{v}	2.934(3)
N1···O3^{ii}	2.840(3)	N2···F	2.954(2)
N1···F	2.853(2)	N2···O3^{ii}	3.027(3)
N1···O4^{iii}	2.896(2)	N2···O1	3.061(3)
N1···O1^{iv}	2.938(2)	N2···O4^{vii}	3.079(3)
N1···O2^{v}	2.948(3)	N2···O5^{iv}	3.088(3)
N2···O1^{iv}	2.857(2)	N2···F^{vii}	3.149(2)
N2···O4^{vi}	2.893(2)		

Symmetry codes

i	$(x,\frac{1}{2}-y,-\frac{1}{2}+z)$	v	$(x-1,y,z)$
ii	$(x-1,\frac{1}{2}-y,\frac{1}{2}+z)$	vi	$(\bar{x},-\frac{1}{2}+y,1\frac{1}{2}-z)$
iii	$(\bar{x},-\frac{1}{2}+y,\frac{1}{2}-z)$	vii	$(x,\frac{1}{2}-y,\frac{1}{2}+z)$
iv	$(\bar{x},\bar{y},1-z)$		

As is evident from Fig. 1 the anions in $(NH_4)_2[VFO(O_2)_2]$ form zigzag chains extending along the crystallographic *c*-direction. The double-bonded oxygen atom, O5, in one $VFO(O_2)_2^{2-}$ unit is linked to the vanadium atom in the next unit *via* a long bond and occupies the apical *trans* position in that unit, the O=V···O angle being 174.8(1)°. Each unit can be described as a pentagonal pyramid. Vanadium can thus be described as being seven-coordinated with pentagonal-bipyramidal geometry in $(NH_4)_2[VFO(O_2)_2]$, while it is six-coordinated with pentagonal-pyramidal geometry in both $K_2[VFO(O_2)_2]$,[3] and $Cs_2[VFO(O_2)_2]$.[24] The r.m.s. deviation of the atoms defining the equatorial pentagonal plane is 0.040 Å and the vanadium atom is displaced 0.364 Å from this plane in the direction of the double-bonded oxygen atom. The neighbouring pentagonal planes form an angle of 21.7° with one another and the V=O···V angle is 157.10(8)°.

The V=O bond length, 1.613(1) Å, is close to the average value, 1.609(7) Å (r.m.s. deviation is given in parenthesis), calculated from data for 11 peroxovanadates (see Table 4 in Ref. 1 and Table 3 in Ref. 12).[1,3,12–20] The $V-F_{equatorial}$ bond length, 1.929(1) Å, is very near the average of the value 1.958(1) Å observed in $(NH_4)_3[VF_2O(O_2)_2]$,[1] and the values 1.900(5)–1.906(3) Å found in $K_2[VFO(O_2)_2]$.[3] This agrees well with the observation that the coordination polyhedron in $(NH_4)_2[VFO(O_2)_2]$ is intermediate between those in $(NH_4)_3[VF_2O(O_2)_2]$ and $K_2[VFO(O_2)_2]$ (see below). The O–O bond lengths, 1.460(2) and 1.462(2) Å, agree well with the average value, 1.464(6) Å,[a] calculated from data for the above-mentioned 11 peroxovanadates.[1,3,12–20]

The two *trans* $V-O_{peroxo}$ bonds V–O1 and V–O4, 1.905(1) and 1.903(1) Å, are significantly longer than the two *cis* $V-O_{peroxo}$ bonds, 1.874(2) and 1.880(2) Å. A similar asymmetry was observed in $(NH_4)_3[VF_2O(O_2)_2]$, the two *trans* $V-O_{peroxo}$ bond lengths being 1.921(2) and 1.927(2) Å and the *cis* $V-O_{peroxo}$ bond lengths being 1.890(2) and 1.887(2) Å.[1] The $V-O_{peroxo}$ bonds are, on the average, 0.015 Å longer in

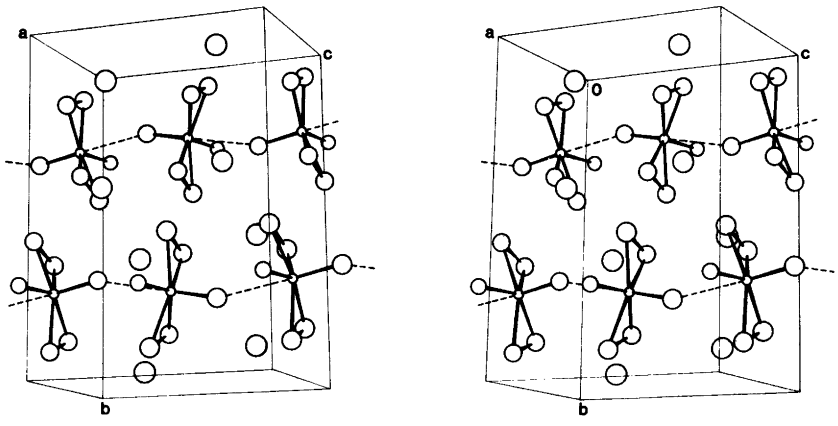

Fig. 1. Stereoscopic drawing of the unit cell of $(NH_4)_2[VFO(O_2)_2]$.

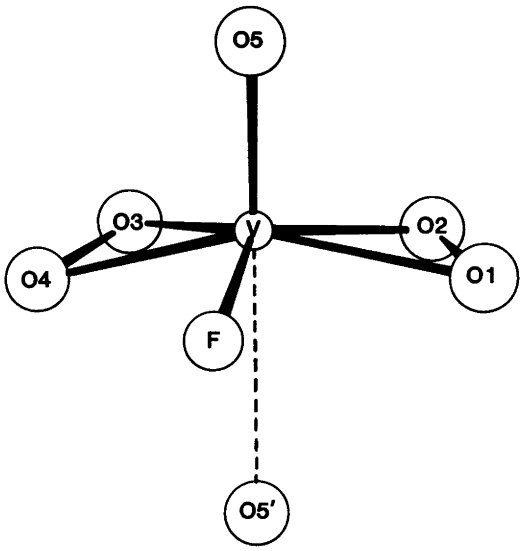

Fig. 2. The configuration of ligands about vanadium. O5′ is the double-bonded oxygen atom in the neighbouring $VFO(O_2)_2^{2-}$ unit.

$(NH_4)_3[VF_2O(O_2)_2]$ than in $(NH_4)_2[VFO(O_2)_2]$, and is probably, like the 0.029 Å elongation of the $V-F_{equatorial}$ bond, a consequence of the closer contact between vanadium and the apical atom *trans* to the double-bonded oxygen atom in $(NH_4)_3[VF_2O(O_2)_2]$. Other examples of $V-O_{peroxo}$ bond asymmetry can be found in $(NH_4)_4[O\{VO(O_2)_2\}_2]$,[20] $K_3[VO(O_2)_2(C_2O_4)]\cdot H_2O$,[15] $(C_{10}H_9N_2)[H\{VO(O_2)_2(C_{10}H_8N_2)\}_2]\cdot xH_2O_2\cdot(6-x)H_2O$,[13] and $(C_{10}H_9N_2)[VO(O_2)_2(C_{10}H_8N_2)]\cdot(3+x)H_2O_2\cdot(2-x)H_2O$.[14] For further comparison between coordination geometries for peroxovanadates, reference is made to Table 4 in Ref. 1 and Table 3 in Ref. 12.

Peroxometallates with heavier elements like niobium, molybdenum and tungsten are usually seven- or eight-coordinated, while vanadium exhibits six-, seven- or eight-coordination in peroxovanadates. Pure six-coordination is unusual even in peroxovanadates and has only been observed in $K_2[VFO(O_2)_2]$,[3] $Cs_2[VFO(O_2)_2]$,[24] and $NH_4[VO(O_2)_2(NH_3)]$;[17] these compounds contain only monodentate ligands, disregarding the peroxo groups. In peroxovanadates with polydentate ligands like oxalate,[15,19] 2,2′-bipyridine,[12–14,18,19] pyridine-2-carboxylate,[12,21] and pyridine-2,6-dicarboxylate[16,22] seven-coordination is usually achieved, while vanadium is eight-coordinated in $(NH_4)_3[V(O_2)_4]$.[22] There is a tendency for vanadium to become seven-coordinated in diperoxovanadates, examples being $(NH_4)_2[VFO(O_2)_2]$, $(NH_4)_4[O\{VO(O_2)_2\}_2]$,[20,23] and $(NH_4)_3[VF_2O(O_2)_2]$.[1] The latter is unusual; it is hitherto the sole example of a peroxovanadate with only monodentate ligands, disregarding the peroxo groups, with an unshared atom occupying the second apical position of the pentagonal-bipyramidal coordination polyhedron. Obviously, there is a substantial change in coordination in going from $K_2[VFO(O_2)_2]$ *via* $(NH_4)_2[VFO(O_2)_2]$ and $(NH_4)_4[O\{VO(O_2)_2\}_2]$, being intermediate, to $(NH_4)_3[VF_2O(O_2)_2]$. The connection between these peroxovanadates has been further discussed in Refs. 1, 3 and 20.

As a consequence of the chain formation in $(NH_4)_2[VFO(O_2)_2]$ the thermal motion of the double-bonded oxygen atom should be considerably less in the chain direction (approximately the *c*-direction); this was in fact observed, the U_{33}-value being 0.015, which is the least U_{ii}-value observed in the present case. Moreover, the V=O stretching mode in the IR-spectrum of $(NH_4)_2[VFO(O_2)_2]$ should be different from the ν(V=O)-value in $K_2[VFO(O_2)_2]$; this was also observed by Schwendt *et al.*[2]

Acknowledgement. We wish to thank F. K. Leif Andersen for programming help.

REFERENCES

1. Stomberg, R. *Acta Chem. Scand. A 38* (1984) 541.
2. Schwendt, P. and Joniaková, D. *Polyhedron 3* (1984) 287.
3. Stomberg, R. *Acta Chem. Scand. A 38* (1984) 223.
4. Stomberg, R. and Svensson, I.-B. *Acta Chem. Scand. A 31* (1977) 635.
5. Massa, W. and Pausewang, G. *Mater. Res. Bull. 13* (1978) 361.
6. Stomberg, R. *Acta Chem. Scand. A 35* (1981) 489.
7. Stomberg, R. *Acta Chem. Scand. A 36* (1982) 101.
8. Stomberg, R. *Acta Chem. Scand. A 37* (1983) 523.
9. Cruickshank, D. W. J. *Crystallographic Computing,* Munksgaard, Copenhagen 1970, p. 195.

10. *International Tables for X-Ray Crystallography,* Kynoch Press, Birmingham 1974, Vol. 4.
11. Lindgren, O. *On the Oxygen Coordination of Cerium in Some Sulfates and Chromates,* Diss., Chalmers University of Technology and University of Göteborg, Göteborg 1977.
12. Szentivanyi, H. and Stomberg, R. *Acta Chem. Scand. A 37* (1983) 709.
13. Szentivanyi, H. and Stomberg, R. *Acta Chem. Scand. A 38* (1984) 101.
14. Stomberg, R. and Szentivanyi, H. *Acta Chem. Scand. A 38* (1984) 121.
15. Begin, D., Einstein, F. W. B. and Field, J. *Inorg. Chem. 14* (1975) 1785.
16. Drew, R. E. and Einstein, F. W. B. *Inorg. Chem. 12* (1973) 829.
17. Drew, R. E. and Einstein, F. W. B. *Inorg. Chem. 11* (1972) 1079.
18. Szentivanyi, H. and Stomberg, R. *Acta Chem. Scand. A 37* (1983) 553.
19. Campbell, N. J., Capparelli, M. V., Griffith, W. P. and Skapski, A. C. *Inorg. Chim. Acta 77* (1983) L215.
20. Stomberg, R., Olson, S. and Svensson, I.-B. *Acta Chem. Scand. A 38* (1984) 653.
21. Mimoun, H., Saussine, L., Daire, E., Postel, M., Fischer, J. and Weiss, R. *J. Am. Chem. Soc. 105* (1983) 3101.
22. Svensson, I.-B. *Personal communication.*
23. Svensson, I.-B. and Stomberg, R. *Acta Chem. Scand. 25* (1971) 898.
24. Stomberg, R. and Olson, S. *Acta Chem. Scand. A 38* (1984) 821.

Received April 24, 1984.