Structure and Stereochemistry in *f*-Block Complexes of High Co-ordination Number. Part 4.* The [M(bidentate ligand)$_4$] System: Crystal Structures of Tetrakis(dibenzoylmethanato)-uranium(IV) and -cerium(IV) †

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The crystal structure of [U^{IV}(PhCOCHCOPh)$_4$] has been determined at 295 K from *X*-ray diffraction data refined by least squares to a residual of 0.042 for 2 257 'observed' reflections. Crystals are orthorhombic, space group *Pccn*, with unit-cell dimensions *a* = 10.323(8), *b* = 20.172(15), *c* = 23.65(2) Å, and *Z* = 4; they are isostructural with the previously studied cerium analogue, the eight-co-ordinate uranium atom lying on a crystallographic two-fold axis, with U–O ranging from 2.323(7) to 2.370(6) Å. For the cerium analogue, *a* = 10.29(1), *b* = 20.07(3), and *c* = 23.42(4) Å; *R* = 0.043 for 1 817 'observed' reflections. The corresponding Ce–O distances lie between 2.291(7) and 2.348(6) Å. The stereochemistries of these complexes are close to square antiprismatic with the bidentate ligands spanning opposite square faces, as predicted by electron-pair repulsion theory.

For [M(symmetrical bidentate ligand)$_4$] complexes the available stereochemistries, as predicted by repulsion theory,[1] are based on the D_{2d} dodecahedron and D_{4d} square antiprism extremes, for ligands of small ($b \lesssim 1.1$) and large ($b \gtrsim 1.3$) normalised bites respectively. A full structure determination is available for only one example of the latter, [Nb(Bu^{t}COCHCOBu^t)$_4$] [2] (*b* = 1.28). A number of complexes for which *b* is intermediate between the above values exhibit 'intermediate' stereochemistries.

For [Zr(MeCOCHCOMe)$_4$] [3] and [Zr(PhCOCHCOPh)$_4$],[4] structure determination shows that although *b* is high (1.22), 'intermediate' stereochemistries result. The acetylacetonates of Zr, Ce,[5] and U [6] are isomorphous, *C*2/*c*, with cell volume *U* increasing monotonically (2 294, 2 386, and 2 411 Å^3) and normalised bites decreasing likewise (*b* = 1.22, 1.17, and 1.16). For [Zr(PhCOCHCOPh)$_4$] the space group is $P2_1/c$ and *U* = 4 949 Å^3; cell determinations available for the cerium and uranium analogues [7] indicate a space group *Pccn* and *U* = 4 880 and 4 899 Å^3, values appreciably *less* than that of the zirconium analogue. Brief reports on the structure determination of the cerium derivative indicate square-antiprismatic stereochemistry.[7,8] In view of these anomalies and our current interest in actinoid stereochemistry [9] we have carried out the structure determination of the uranium derivative and, also, a redetermination of the cerium derivative.

Experimental

Tetrakis(dibenzoylmethanato)uranium(IV).—A preparation of this complex has been previously reported.[10]

In the preparation of the present material, dibenzoylmethane (0.9 g, 4.0 mmol) dissolved in the minimum amount of acetone was added to a solution of uranium tetrachloride (0.4 g, 1.0 mmol) in water. To the stirred solution was added a solution of sodium hydroxide (0.16 g, 4.0 mmol) in water (10 cm^3). After 1 h the mixture was extracted with diethyl ether (3 × 20 cm^3) and the ethereal extracts dried (Na_2SO_4) and left to stand overnight. The most concentrated fraction yielded crystals suitable for crystallographic work.

Tetrakis(dibenzoylmethanato)cerium(IV).—A preparation of this complex has been previously reported.[11]

In the present case, cerium(III) nitrate (1.3 g, 3 mmol) and dibenzoylmethane (2 g, 18 mmol) were dissolved in ethanol (50 cm^3), and dilute ammonia added until the solution was just alkaline. The solution was warmed, and the precipitate of tetrakis(dibenzoylmethanato)cerium(IV) filtered off. Crystals were obtained by recrystallising this powder from chloroform–light petroleum (b.p. 60—70 °C).

Crystallography.—For general details of procedure the reader is referred to ref. 9.

Crystal data. $C_{60}H_{44}O_8U$, *M* = 1 131, Orthorhombic, space group *Pccn* (D_{2h}^{10}, no. 56), *a* = 10.323(8), *b* = 20.172(15), *c* = 23.65(2) Å, *U* = 4 925(7) Å^3, D_m = 1.50(1), *Z* = 4, D_c = 1.53 g cm^{-3}, *F*(000) = 2 240, μ_{Mo} = 32.1 cm^{-1}. Specimen: prism, 0.12 × 0.12 × 0.37 mm; $2\theta_{max.}$ = 50°, *N* = 4 428, N_o = 2 257, *R* = 0.042, *R'* = 0.049.

$C_{60}H_{44}CeO_8$, *M* = 1 033, Orthorhombic, space group *Pccn*, *a* = 10.29(1), *b* = 20.07(3), *c* = 23.42(4) Å, *U* = 4 836(4) Å^3, D_m = 1.40(1), *Z* = 4, D_c = 1.42 g cm^{-3}, *F*(000) = 2 104, μ_{Mo} = 10.1 cm^{-1}. Specimen: needle, 0.32 × 0.10 × 0.16 mm; $2\theta_{max.}$ = 50°, *N* = 4 419, N_o = 1 817, *R* = 0.043, *R'* = 0.047.

Abnormal features. In these structures the metal atom lies on a special position and contributes to only one half of the reflections, the other half being weak. Data were collected at a slower scan rate than usual in order to optimise the measurement of the weak reflections. Crystals of the cerium derivative were only obtained at the lower limit of useful size, and the data were less precise than those of the uranium analogue.

Discussion

The structure determinations show that, as expected, tetrakis(dibenzoylmethanato)-uranium(IV) and -cerium(IV) are isomorphous. The unit-cell contents of the uranium derivative are shown in Figure 1 and a projection of a single molecule in Figure 2(*a*). The metal atom lies on a crystallographic two-fold rotor so that one half of the molecule comprises the asymmetric unit; the projection of Figure 2(*a*) is down this axis. Atom co-ordinates are given in Table 1.

Also given, in Figure 2(*b*) for comparison, is a similar projection of the zirconium analogue, derived from the data of

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* For Part 3 see preceding paper.

† Supplementary data available (No. SUP 23491, 35 pp.): thermal parameters, H-atom co-ordinates, phenyl ring geometries and least-squares planes, ligand planes, structure factors. See Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.

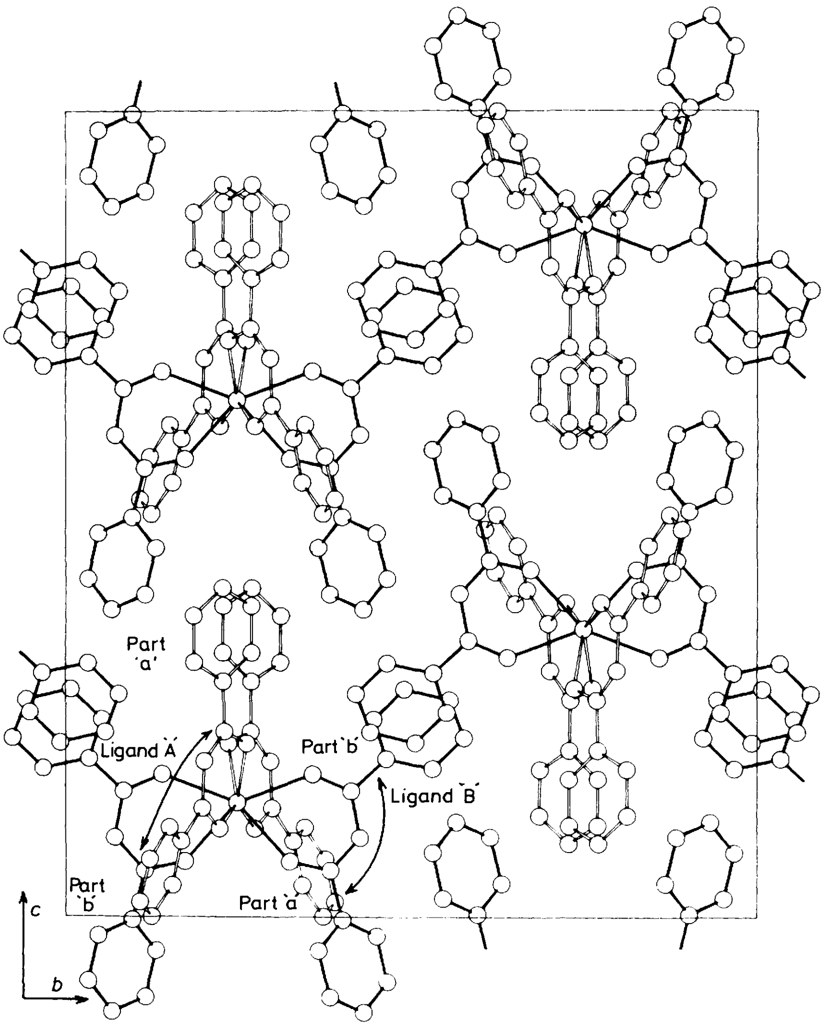


Figure 1. Unit-cell contents of the complex [U(PhCOCHCOPh)$_4$] projected down *a*, showing non-hydrogen atoms and ligand labelling

ref. 4. In this case, the molecule has no crystallographically imposed symmetry, the molecule comprising the asymmetric unit in space group $P2_1/c$; nevertheless, the disposition of the atoms in both the metal-atom environment and the molecule periphery is essentially identical with that found in the uranium derivative. The smaller cell volumes of the cerium and uranium complexes compared with the zirconium complex is confirmed.

Metal–oxygen distances in both cerium and uranium complexes (Table 2) vary significantly, the range of values in each case being about 0.05 Å, and the extremes for the two compounds being in correspondence The mean Ce–O and U–O distances of 2.3_2 and 2.3_4 Å respectively are similar to those found in the acetylacetonate analogues {2.3_2 Å in β-[Ce(acac)$_4$],[5] 2.31 Å in β-[U(acac)$_4$],[6] and 2.40(3) Å for the less precise determination of the structure of α-[Ce(acac)$_4$] [12]}. The angles subtended at the metal by the oxygen atoms of the ligands are (mean) $70._8$° (U), $70._9$° (Ce), and $74._6$° (Zr); in the latter case the metal–oxygen distances are shorter (2.1_7 Å). These parameters are also very similar to those reported for the corresponding acetylacetonates.[3,5,6]

The ligand geometries are relatively imprecise (Table 3) and show no significant changes in distances and angles relative to the free ligand; the latter exists in the solid state as the 'enol' tautomer, with the acidic proton hydrogen bonding the two oxygen atoms of the same molecule. However, a gross change is found in the latter distance; O · · · O in the parent ligand is 2.46 and 2.7_0 Å in the uranium, cerium, and zirconium complexes. In the present uranium complex, the metal atom lies 0.77 and 0.62 Å out of the ligand planes; the corresponding values for the cerium complex are 0.77 and 0.60 Å and for the zirconium 0.71, 0.70, 0.63, and 0.54 Å, with MO$_2$/ligand interplanar fold angles slightly above 20°. Smaller fold angles (8°) are observed in the structures of Cs[M(CF$_3$COCHCOCF$_3$)$_4$] (M = Y, Eu, or Am),[13,14] where the metal atoms are of smaller radius; calculations carried out in conjunction with these studies suggest that fold angles of this magnitude are of such energies as are normally associated with 'packing forces'.

The stereochemistries about the metal atoms of both complexes are close to square antiprisms with the bidentate ligands spanning opposite sides of each square face. A perfect square antiprism is only expected at a normalised bite *b* of 1.19 (calculated for $n = 6$). At other values of the normalised bite the minimum on the potential-energy surface shifts corresponding to creasing across the diagonals of the square (or rectangular) faces with the creation of the more general 'intermediate' structure.[15] However, these structural changes may be obscured by relatively large experimental scatter as the potential-energy surfaces calculated at these values of the

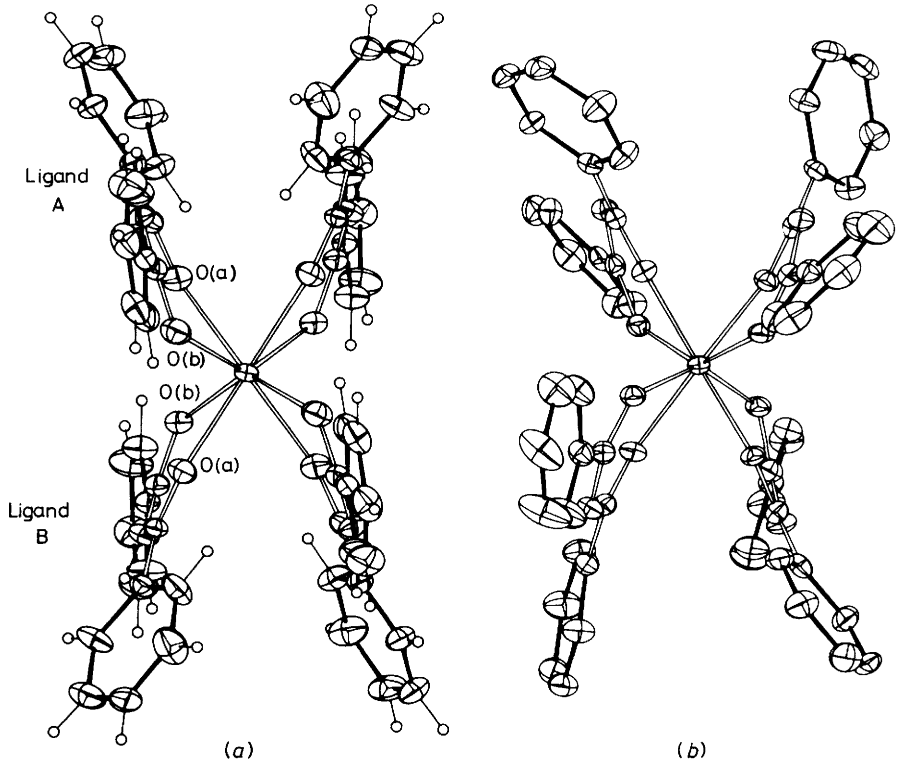
Table 1. Non-hydrogen atomic co-ordinates

	Ligand A			Ligand B		
Atom	*x*	*y*	*z*	*x*	*y*	*z*
(*a*) Complex [U(PhCOCHCOPh)$_4$]						
U	0.250 0(—)	0.250 00(—)	0.142 14(2)			
C(ab)	0.581 2(10)	0.202 2(5)	0.193 5(5)	0.199 7(12)	0.428 0(5)	0.098 5(5)
(*i*) Section a						
O	0.396 8(7)	0.263 2(3)	0.215 7(3)	0.285 0(5)	0.326 2(3)	0.068 9(3)
C	0.499 9(11)	0.231 0(4)	0.230 3(5)	0.240 4(12)	0.384 7(4)	0.057 8(4)
C(1)	0.526 3(11)	0.229 6(5)	0.293 0(5)	0.233 2(11)	0.402 5(5)	−0.003 5(5)
C(2)	0.617 4(12)	0.187 4(6)	0.316 6(6)	0.307 4(12)	0.367 9(6)	−0.041 9(6)
C(3)	0.639 1(15)	0.186 7(7)	0.374 1(6)	0.301 9(16)	0.384 0(7)	−0.099 5(5)
C(4)	0.573 2(17)	0.228 7(7)	0.408 5(5)	0.218 8(13)	0.432 9(8)	−0.118 0(5)
C(5)	0.481 0(16)	0.270 5(6)	0.386 4(6)	0.147 3(15)	0.467 1(7)	−0.080 0(6)
C(6)	0.456 7(12)	0.270 8(5)	0.328 6(6)	0.152 8(13)	0.452 2(6)	−0.023 4(5)
(*ii*) Section b						
O	0.457 9(7)	0.224 6(3)	0.109 7(3)	0.222 2(6)	0.359 2(3)	0.177 2(3)
C	0.561 2(10)	0.199 5(5)	0.135 2(5)	0.191 4(10)	0.415 4(5)	0.156 4(5)
C(1)	0.656 6(11)	0.168 7(5)	0.094 0(5)	0.141 0(10)	0.465 8(5)	0.196 8(5)
C(2)	0.781 2(10)	0.151 8(7)	0.111 0(6)	0.143 3(13)	0.532 8(5)	0.184 3(5)
C(3)	0.862 2(12)	0.122 7(7)	0.071 7(9)	0.087 2(15)	0.577 7(6)	0.222 6(7)
C(4)	0.822 6(16)	0.108 6(8)	0.018 9(7)	0.029 3(13)	0.557 6(7)	0.270 0(7)
C(5)	0.700 0(14)	0.125 6(8)	0.000 7(7)	0.030 6(16)	0.492 1(7)	0.283 4(6)
C(6)	0.617 8(11)	0.155 8(6)	0.039 4(5)	0.089 0(14)	0.447 3(6)	0.245 9(6)
(*b*) Complex [Ce(PhCOCHCOPh)$_4$]						
Ce	0.250 00(—)	0.250 00(—)	0.142 03(3)			
C(ab)	0.579 3(9)	0.201 6(5)	0.190 7(5)	0.198 9(9)	0.428 5(4)	0.100 0(4)
(*i*) Section a						
O	0.396 7(6)	0.264 4(3)	0.214 6(3)	0.286 4(5)	0.326 4(3)	0.070 4(3)
C	0.498 3(4)	0.232 4(4)	0.229 5(4)	0.239 5(13)	0.383 6(4)	0.058 2(3)
C(1)	0.525 9(10)	0.231 1(4)	0.292 1(5)	0.235 5(13)	0.402 3(4)	−0.003 4(4)
C(2)	0.616 5(11)	0.188 3(6)	0.314 3(5)	0.307 2(12)	0.367 7(5)	−0.041 6(5)
C(3)	0.636 8(14)	0.187 7(7)	0.372 6(5)	0.302 7(13)	0.383 3(7)	−0.098 8(5)
C(4)	0.571 6(14)	0.229 9(5)	0.408 4(4)	0.222 3(14)	0.432 6(6)	−0.117 6(5)
C(5)	0.479 6(12)	0.271 1(5)	0.384 8(5)	0.148 1(13)	0.467 4(6)	−0.080 4(6)
C(6)	0.454 0(10)	0.271 8(4)	0.327 2(5)	0.154 6(12)	0.451 6(6)	−0.023 5(5)
(*ii*) Section b						
O	0.456 9(6)	0.223 0(3)	0.109 2(3)	0.217 6(5)	0.357 8(3)	0.178 3(2)
C	0.559 2(9)	0.198 8(4)	0.132 4(4)	0.190 5(9)	0.413 8(5)	0.157 5(4)
C(1)	0.655 2(10)	0.168 2(5)	0.092 3(5)	0.139 0(10)	0.466 0(5)	0.196 9(4)
C(2)	0.781 1(8)	0.152 6(5)	0.109 4(5)	0.143 1(11)	0.532 3(5)	0.185 8(4)
C(3)	0.863 2(11)	0.122 9(7)	0.070 6(7)	0.088 3(14)	0.577 4(6)	0.222 6(6)
C(4)	0.824 4(15)	0.109 4(7)	0.017 3(6)	0.027 9(12)	0.557 9(6)	0.271 5(6)
C(5)	0.699 7(14)	0.124 1(7)	−0.000 7(6)	0.030 2(15)	0.492 6(7)	0.284 6(5)
C(6)	0.615 7(10)	0.155 1(6)	0.038 0(5)	0.086 5(14)	0.447 4(6)	0.247 2(6)

Table 2. Metal-atom environment. The first column in the matrix is the M–O distance (Å); the other entries are the angles (°) subtended by the relevant atoms. Primed atoms are generated by the intramolecular two-fold axis

U	*r*	O(Ab)	O(Ba)	O(Bb)	O(Aa′)	O(Ab′)	O(Ba′)	O(Bb′)
O(Aa)	2.323(7)	70.9(2)	112.2(2)	73.2(2)	82.9(3)	145.1(2)	136.9(2)	76.5(2)
O(Ab)	2.336(7)		76.1(2)	115.5(2)	145.1(2)	141.6(2)	75.8(2)	78.5(2)
O(Ba)	2.345(7)			70.6(2)	136.9(2)	75.8(2)	84.7(2)	148.1(2)
O(Bb)	2.370(6)				76.5(2)	78.5(2)	148.1(2)	139.1(2)
O(Aa′)						70.9(2)	112.2(2)	73.2(2)
O(Ab′)							76.1(2)	115.5(2)
O(Ba′)								70.6(2)

Ce	*r*	O(Ab)	O(Ba)	O(Bb)	O(Aa′)	O(Ab′)	O(Ba′)	O(Bb′)
O(Aa)	2.291(7)	70.8(2)	110.4(2)	73.1(2)	84.3(2)	144.9(2)	137.0(2)	75.8(2)
O(Ab)	2.329(6)		76.5(2)	117.6(2)	144.9(2)	141.4(2)	75.7(2)	77.0(2)
O(Ba)	2.303(6)			70.9(2)	137.0(2)	75.7(2)	86.5(2)	148.6(2)
O(Bb)	2.348(6)				75.8(2)	77.0(2)	148.6(2)	137.6(2)
O(Aa′)						70.8(2)	110.4(2)	73.1(2)
O(Ab′)							76.5(2)	117.6(2)
O(Ba′)								70.9(2)



(*a*) (*b*)

Figure 2. A single molecule, projected down its two-fold axis showing 20% thermal ellipsoids, for the non-hydrogen atoms of [U(PhCOCHCOPh)$_4$] (*a*) and [Zr(PhCOCHCOPh)$_4$] (*b*)[4]

normalised bite are fairly flat, corresponding to the low energy required to crease these faces.

Least-squares planes through these ' square faces ' are given in SUP 23491. Alternatively, the creasing of these faces can be measured by α, the angle the metal-ligand bonds make to the pseudo-four-fold axis of the antiprism:[15] α = 56.1 and 57.8 for the uranium complex and 55.1 and 58.8° for the cerium complex. These values may be compared with α = 57.1° calculated for [M(unidentate ligand)$_8$] (n = 6) and $\alpha \sim$ 58 and 55° for [M(bidentate ligand)$_4$] at a normalised bite of b = 1.16 as in the present complexes.

Table 3. Ligand geometries; distances in Å, angles in degrees

	Ligand section			
	Aa	Ab	Ba	Bb
(*a*) Complex [U(PhCOCHCOPh)$_4$]				
O–C	1.29(1)	1.33(1)	1.29(1)	1.28(1)
C–C(1)	1.51(2)	1.52(2)	1.50(1)	1.49(1)
C–C(ab)	1.34(2)	1.39(2)	1.37(1)	1.40(2)
O···O	2.70(1)		2.72(1)	
U–O–C	132.7(6)	132.3(6)	133.8(6)	136.2(6)
O–C–C(1)	114.9(9)	112.7(9)	115.7(8)	116.6(9)
O–C–C(ab)	123.9(11)	123.6(9)	123.5(9)	121.5(9)
C(1)–C–C(ab)	121.2(10)	123.7(9)	120.9(9)	121.8(9)
C–C(ab)–C	124.5(10)		126.4(9)	
(*b*) Complex [Ce(PhCOCHCOPh)$_4$]				
O–C	1.28(1)	1.28(1)	1.28(1)	1.26(1)
C–C(1)	1.49(2)	1.49(1)	1.49(1)	1.49(1)
C–C(ab)	1.38(1)	1.38(2)	1.40(1)	1.38(1)
O···O	2.68(1)		2.70(1)	
Ce–O–C	132.8(6)	134.5(6)	134.4(6)	135.6(6)
O–C–C(1)	115.7(9)	115.7(9)	117.0(8)	117.7(8)
O–C–C(ab)	122.8(9)	121.8(9)	122.4(8)	123.8(9)
C(1)–C–C(ab)	121.5(9)	122.5(9)	120.5(9)	118.4(9)
C–C(ab)–C	125.3(9)		124.4(8)	

References

1 D. L. Kepert, ' Inorganic Stereochemistry,' Springer, Berlin, 1981.
2 T. J. Pinnavia, B. L. Barnett, G. Podolsky, and A. Tulinsky, *J. Am. Chem. Soc.*, 1975, **97**, 2712.
3 J. V. Silverton and J. L. Hoard, *Inorg. Chem.*, 1963, **2**, 243.
4 H. K. Chun, W. L. Steffen, and R. C. Fay, *Inorg. Chem.*, 1979, **18**, 2458.
5 H. Titze, *Acta Chem. Scand.*, 1969, **23**, 399.
6 H. Titze, *Acta Chem. Scand.*, 1970, **24**, 405.
7 L. Wolf and H. Barnighausen, *Acta Crystallogr.*, 1960, **13**, 778.
8 H. Barnighausen, *Z. Kristallogr. Kristallgeom.*, *KristallPhys.*, *Kristallchem.*, 1971, **134**, 449.
9 D. L. Kepert, J. M. Patrick, and A. H. White, *J. Chem. Soc., Dalton Trans.*, 1983, 381.
10 H. I. Schlesinger, H. C. Brown, J. J. Katz, S. Archer, and R. A. Lad, *J. Am. Chem. Soc.*, 1953, **75**, 2446.
11 L. Sacconi and G. Ercoli, *Gazz. Chim. Ital.*, 1949, **79**, 731.
12 B. Matkovic and D. Grdenić, *Acta Crystallogr.*, 1963, **16**, 456.
13 M. J. Bennett, F. A. Cotton, P. Legzdins, and S. J. Lippard, *Inorg. Chem.*, 1968, **7**, 1770.
14 J. H. Burns and M. D. Danford, *Inorg. Chem.*, 1969, **8**, 1780.
15 D. L. Kepert, *Prog. Inorg. Chem.*, 1978, **24**, 179.

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