Stereochemistry of Seven-co-ordinate Compounds Bis(bidentate ligand)-tris(unidentate ligand)metal

By **David L. Kepert**, School of Chemistry, University of Western Australia, Nedlands 6009, Western Australia

Repulsion-energy calculations have been used to examine the stereochemistry of compounds of the type [M-(bidentate)$_2$(unidentate)$_3$]$^{x\pm}$. For bidentate ligands having small normalised bites ($b < 1{\cdot}1$), it is predicted that the only stable stereochemistry, (I), will be the pentagonal bipyramid with the bidentate ligands spanning two of the equatorial edges, the symmetry being C_{2v}. This prediction is in excellent agreement with known structures. As the normalised bite is increased, the pentagonal plane progressively distorts with loss of the mirror planes but retention of the two-fold axis, with the polyhedron approaching first a capped trigonal prism with the bidentate ligands spanning opposite triangular edges of the triangular prism and secondly a pentagonal bipyramid with the bidentate ligands spanning edges linking axial and equatorial sites. Compounds with stereochemistry (II) may be expected to occur with bidentate ligands having normalised bites above *ca.* 1·3. Stereochemistry (II) also has a two-fold axis, and again the polyhedron chosen to represent the structure best depends on the value of the normalised bite. The predictions are in agreement with experiment. A third minimum on the potential-energy surface becomes of sufficiently low energy to be considered as a possible stereochemistry for normalised bites in the region $b \sim 1{\cdot}2$—$1{\cdot}3$. This stereochemistry, (III), contains a mirror plane and is well represented by a capped trigonal prism with the bidentate ligands again spanning two of the triangular edges of the prism.

It has previously been shown that the expected stereochemistries for seven-co-ordinate compounds of the types [M(bidentate)$_3$(unidentate)] [1,2] and [M(bidentate)(unidentate)$_5$] [3] are not necessarily the same as those expected for compounds containing only unidentate ligands. The predicted stereochemistries, however, agree well with molecules of known crystal structure. This work is now extended to seven-co-ordinate complexes containing two bidentate ligands.

METHOD

Each stereochemistry of the type [M(bidentate)$_2$(unidentate)$_3$] is defined by nine angular co-ordinates, two for each unidentate ligand plus three for each bidentate ligand, the fourth being calculated from the other three and the normalised bite of the bidentate ligand, b, minus three which are fixed when defining the co-ordinate axes. The repulsion-energy coefficients X, which are a direct measure of the stability of the particular stereochemistry, were calculated as before,[1,4] the minima on the potential-energy surfaces being located to the nearest 0·1° in each of the angular co-ordinates. The normalised bite of the bidentate ligands b was varied from 0 to 1·5. The previous custom of using values of 1, 6, and 12 for n in the repulsive-energy function was continued.

RESULTS

Three separate minima occurred on the potential-energy surfaces, which will be described in turn.

Stereochemistry (I).—Stereochemistry (I) occurred as a minimum over the entire range b = 0—1·5 and n = 1, 6, and 12. In all cases the stereochemistry contains a two-fold axis passing through the metal atom M. The axes and atom labelling are defined in Figure 1. The unidentate ligand A is placed at the 'North Pole' along the two-fold axis with $\phi_A = 0$, the 'longitudes' being defined relative to $\theta_B = 0$. The variation of the ϕ_B, ϕ_D, and ϕ_E angular co-ordinates with normalised bite are shown in Figure 2(*a*) (with $\phi_A = 0$, $\phi_C = \phi_B$, $\phi_F = \phi_D$, and $\phi_G = \phi_E$), and the corresponding θ_D and θ_E angular co-ordinates in Figure 2(*b*) (with $\theta_B = 0$, $\theta_C = 180$, $\theta_F = \theta_D + 180$, and $\theta_G = \theta_E + 180°$).

When the normalised bite of the bidentate ligand was zero, $\theta_D = \theta_E = 90°$, and the structure is a distorted trigonal bipyramid with each coalesced bidentate ligand occupying one of the equatorial sites. As the normalised bite progressively increased, θ_D and θ_E remained equal to 90°, with the formation of a planar pentagonal bipyramid [Figure 1(*a*)]. The potential-energy surfaces were very flat in the direction of increasing θ_D, the increase in that part of the repulsion-energy coefficient associated with atoms B and D being partially balanced by the decrease in that portion associated with atoms A and E. This increase in θ_D corresponds to a buckling of the pentagonal plane.

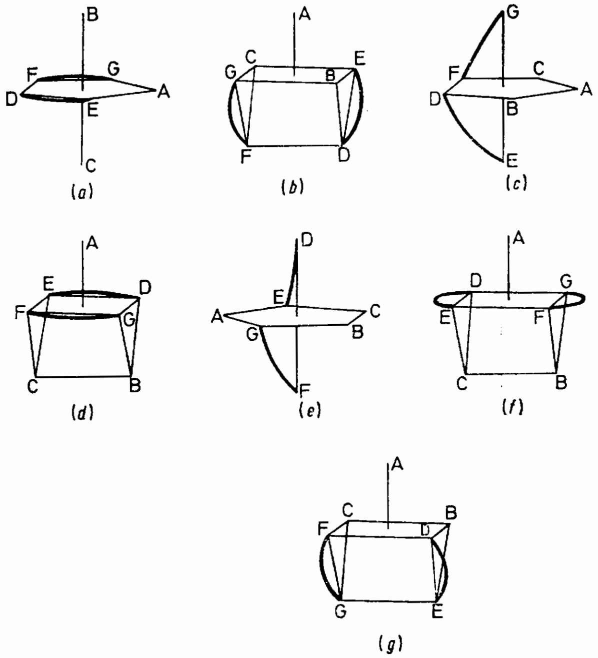

Figure 1 Stereochemistry of compounds [M(bidentate)$_2$(unidentate)$_3$]: (I), (*a*) $b \sim 1{\cdot}00$, (*b*) $b \sim 1{\cdot}23$, (*c*) $b \sim 1{\cdot}41$; (II), (*d*) $b \sim 1{\cdot}30$, (*e*) $b \sim 1{\cdot}41$, (*f*) $b \sim 1{\cdot}50$; (III), (*g*) $b \sim 1{\cdot}30$

---

[1] D. L. Kepert, *J.C.S. Dalton*, 1974, 617.

[2] D. L. Kepert, *Inorg. Chem.*, 1974, **13**, 2754, 2758.

[3] J. C. Dewan, K. Henrick, D. L. Kepert, K. R. Trigwell, A. H. White, and S. B. Wild, *J.C.S. Dalton*, 1975, 546.

[4] D. L. Kepert, *J.C.S. Dalton*, preceding paper.

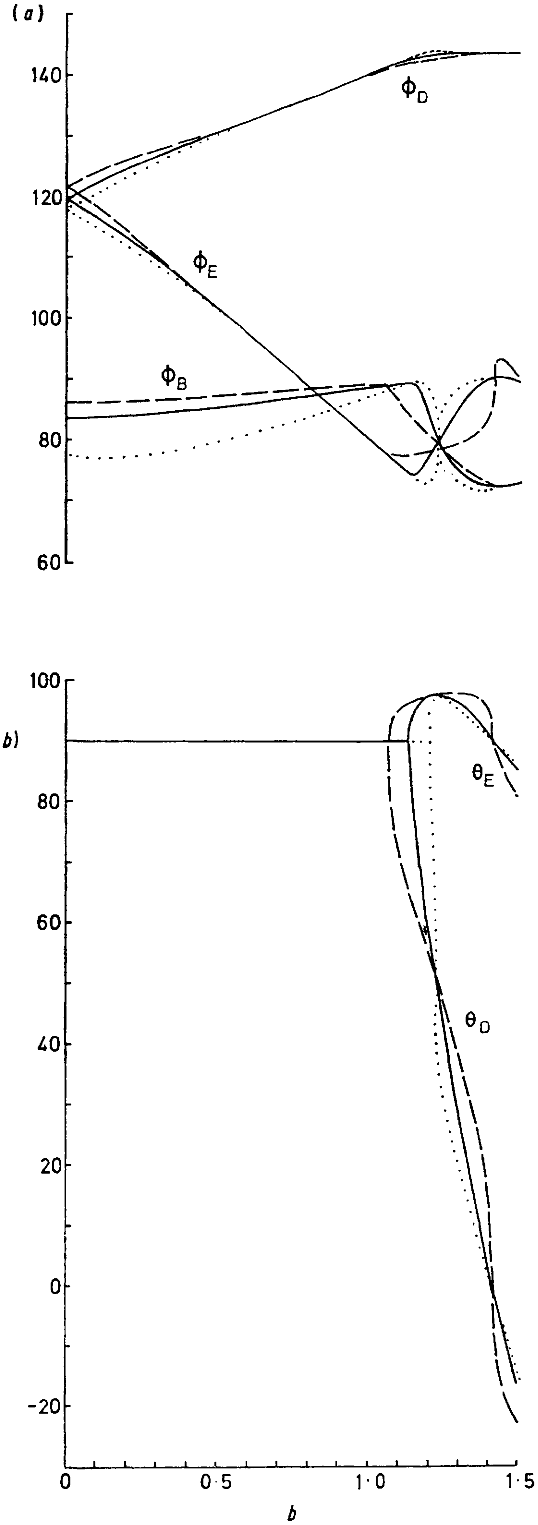

FIGURE 2 Angular co-ordinates (°) for stereochemistry (I) of [M(bidentate)$_2$(unidentate)$_3$] as a function of normalised bite *b*: (· · · ·), $n = 1$; (——), $n = 6$; (— — —), $n = 12$

As the normalised bidentate bite was further increased ($b > 1{\cdot}20$ for $n = 1$, $b > 1{\cdot}14$ for $n = 6$, and $b > 1{\cdot}07$ for $n = 12$), the minima on the potential-energy surfaces moved to lower θ_D (Figure 2). It may be noted that this buckling of the pentagonal plane commences before the normalised bite reaches $b = 2 \sin 36° = 1{\cdot}18$, corresponding to the bidentate ligands spanning the edges of a planar regular pentagon, illustrating the inadequacy of predicting stereochemistries merely by the matching of bidentate ligand bites to edges of polyhedra which may be appropriate for [M(unidentate)$_7$]. Figure 2 shows that at $b \sim 1{\cdot}23$, $\phi_B \sim \phi_E \sim 80$, $\theta_D \sim 51$, $\theta_E \sim 97$, and $\phi_D \sim 143°$, and the stereochemistry corresponds fairly closely to the capped trigonal prism shown in Figure 1(*b*). The potential-energy surfaces remained fairly flat in the direction of increasing or decreasing θ_D.

On further increasing the normalised bite, ϕ_B and θ_E went through maxima, and ϕ_E through a minimum, until at $b = 2^{\frac{1}{2}} = 1{\cdot}414$, $\phi_B = 72$, $\phi_D = 144$, $\phi_E = 90$, $\theta_D = 0$, and $\theta_E = 90°$, the stereochemistry corresponding to the pentagonal bipyramid shown in Figure 1(*c*). At very high values of the bidentate ligand bite θ_D and θ_E continued to decrease so that the projections of the B and C unidentate ligands were directed towards the bidentate ligands, rather than between them as found for lower values of *b*.

Stereochemistry (II).—Stereochemistry (II) occurred as a minimum only at relatively large values of the bidentate ligand normalised bite ($b > 1{\cdot}20$ for $n = 1$, $b > 1{\cdot}28$ for $n = 6$, and $b > 1{\cdot}30$ for $n = 12$). This stereochemistry also always contains a two-fold axis, but in this case the unidentate ligands are arranged on both sides of the pair of bidentate ligands, in contrast to stereochemistry (I) where all unidentate ligands are on the same side of the pair of bidentate ligands. The axes and atom labelling are similar to those used for stereochemistry (I) and are defined in Figure 1. The variation of the ϕ_B, ϕ_D, and ϕ_E angular co-ordinates with normalised bite are shown in Figure (3*a*) (with $\phi_A = 0$, $\phi_C = \phi_B$, $\phi_F = \phi_D$, and $\phi_G = \phi_E$ as before), and the corresponding θ_D and θ_E angular co-ordinates in Figure 3(*b*) (with $\theta_B = 0$, $\theta_C = 180$, $\theta_F = \theta_D + 180$, and $\theta_G = \theta_E + 180°$ as before). For relatively low values of the normalised bidentate ligand bite ($b = 1{\cdot}20$—$1{\cdot}26$ for $n = 1$, $b = 1{\cdot}28$—$1{\cdot}34$ for $n = 6$, and $b = 1{\cdot}30$—$1{\cdot}49$ for $n = 12$), $\phi_D = \phi_E$, $\theta_D + \theta_E = 180°$, and the stereochemistry corresponds to the capped trigonal prism shown in Figure 1(*d*).

For $n = 1$, as the bidentate ligand bite was progressively increased from 1·26, the plane containing the two bidentate ligands puckered by increasing ϕ_D and decreasing ϕ_E, and θ_D and θ_E simultaneously increased so that the two bidentate ligands rotated about the two-fold axis. At $b = 2^{\frac{1}{2}} = 1{\cdot}414$, $\phi_B = 144$, $\phi_D = 90$, $\phi_E = 72$, $\theta_D = 90$, and $\theta_E = 180°$, and the pentagonal bipyramid shown in Figure 1(*e*) was reached. As *b* was increased further, θ_D and θ_E continued to increase until eventually the capped trigonal prism shown in Figure 1(*f*) was reached, where the projections of the unidentate ligands are directed towards the midpoints of the bidentate ligands, rather than midway between the bidentate ligands as is observed at low values of *b*. In the cases of $n = 6$ and 12, where it is more difficult for the ligand atoms to push past each other, the range of existence of the stereochemistry characteristic of low normalised bites ($n = 6$, $b < 1{\cdot}42$; $n = 12$, $b < 1{\cdot}49$) overlapped with that characteristic of high normalised bites ($n = 6$, $b > 1{\cdot}34$; $n = 12$, $b > 1{\cdot}06$), with a low saddle existing between the two discrete minima. This relation between the two alternative capped trigonal prisms and the intervening pentagonal bipyramid as a function of *b* and *n* is exactly analogous to that found for compounds of the type [M(bidentate)$_3$(unidentate)].[2]

Stereochemistry (III).—Stereochemistry (III) in all cases contains a mirror plane. The axes and atom labels are shown in Figure 1(*g*); $\phi_A = 0$, $\phi_C = \phi_B$, $\phi_F = \phi_D$, $\phi_G = \phi_E$, $\theta_C = -\theta_B$, $\theta_F = -\theta_D$, and $\theta_G = -\theta_E$. The angular parameters (Figure 4) show that in all cases $\phi_D \sim \phi_B$, and the stereochemistry may be represented by the capped trigonal prism shown in Figure 1(*g*).

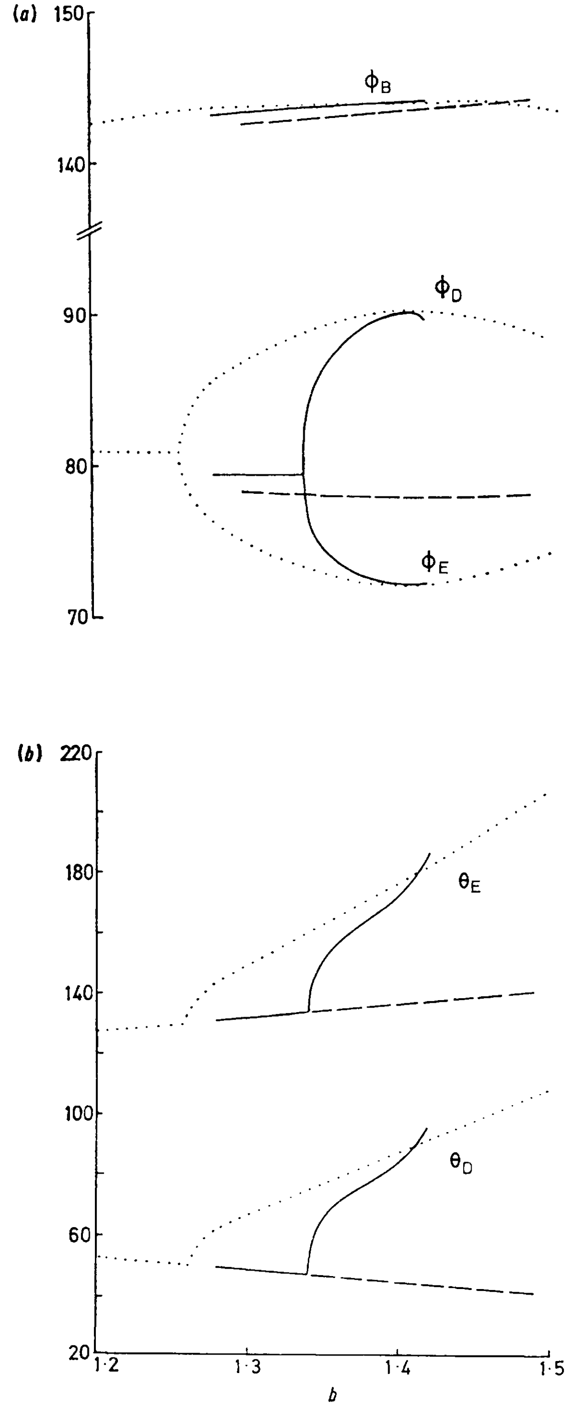

FIGURE 3 Angular co-ordinates (°) for stereochemistry (II) of [M(bidentate)$_2$(unidentate)$_3$] as a function of normalised bite *b*: (· · · ·), $n = 1$; (——), $n = 6$ (low normalised bites only); (— — —), $n = 12$ (low normalised bites only)

The relative repulsion-energy coefficients for these three stereochemistries, normalised to those of (I) are shown in Figure 5 for $n = 6$. Similar curves were obtained for $n = 1$ and 12.

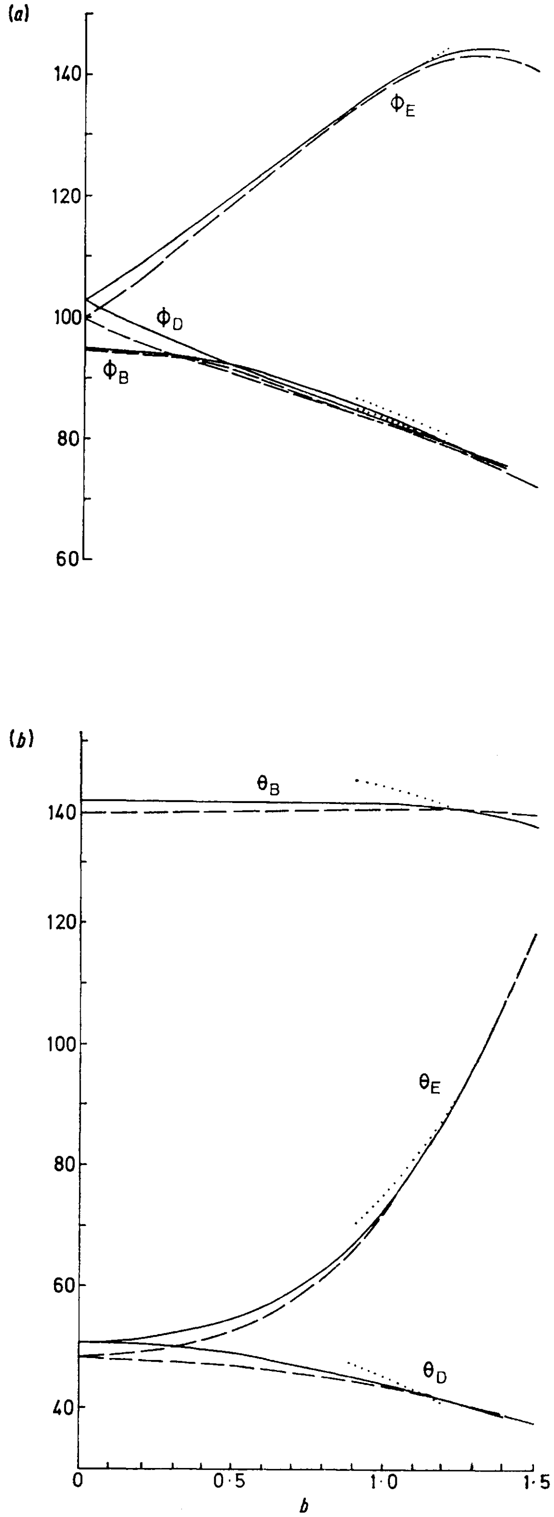

FIGURE 4 Angular co-ordinates (°) for stereochemistry (III) of [M(bidentate)$_2$(unidentate)$_3$] as a function of normalised bite *b*: (· · · ·), $n = 1$; (——), $n = 6$; (— — —), $n = 12$

DISCUSSION

Stereochemistry (I) occurs as a relatively low energy minimum over the entire range of normalised bidentate ligand bite. Stereochemistry (II) occurs as a minimum of comparable stability only above normalised-bite values of *ca.* 1·3. Compounds of stereochemistry (III) would only be expected for normalised-bite values in the approximate range 1·2—1·3. Further information concerning the relative stability of these three stereochemistries can be gained by remembering that the donor atoms of the unidentate and bidentate ligands are necessarily different. Comparison of these structures shows that stereochemistry (II) separates the unidentate ligands from each other, and also the bidentate ligands from each other, more effectively than do (I) or (III). Stereochemistry (II) will therefore be increasingly stable, relative to that shown in Figure 5, as the chemical differences between the unidentate and bidentate ligands increase.

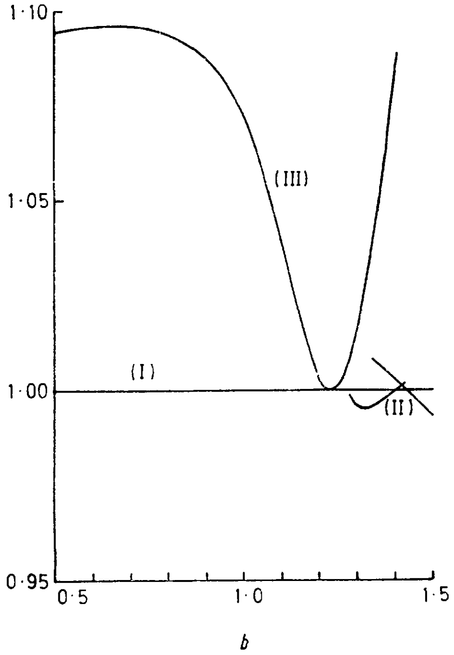

FIGURE 5 Repulsion-energy coefficients X normalised to stereochemistry (I) ($n = 6$)

The Table lists the stereochemistries known for all molecules of stoicheiometry [M(bidentate)$_2$(unidentate)$_3$]. The observed stereochemistries are in excellent agreement with the above predictions. All compounds possessing bidentate ligands in the b range 0·7—1·2 have the pentagonal-bipyramidal structure of stereochemistry (I) as predicted. Small distortions from the planar pentagonal-bipyramidal structure are due almost completely to deviations in θ_D from 90°; of the six compounds listed in the Table with three equivalent unidentate and two equivalent bidentate ligands, θ_D is in the range 90—96° (average 92°). The three compounds with bidentate ligands of larger normalised bites all have stereochemistry (II). The stabilisation of this stereochemistry compared with (I) and (III) is at least partly related to the chemical differences between the unidentate and bidentate ligands.

Stereochemistries of compounds [M(bidentate)$_2$(unidentate)$_3$][a]

Compound	b	Stereo-chemistry	Ref.
$[Cr(O_2)_2(NH_3)_3]$	0·76	(I)	*c*
$K_3[Cr(O_2)_2(CN)_3]$	0·77	(I)	*d*
$[Mo(O_2)_2O\{OP(NMe_2)_3\}(py)]$	0·75	(I)	*e*
$[Mo(O_2)_2\{OP(NMe_2)_3\}(OH_2)]$	0·77	(I)	*e*
$[Cd(NO_3)_2(quin)_2(OH_2)]$	0·87	(I)	*f*
$[Cd(NO_3)_2(py)_3]$	0·87	(I)	*g*
$[Zn(NO_3)_2(py)_3]$	0·90	(I)	*h*
$[Co(NO_3)_2(py)_3]$	0·94	(I)	*h*
$[V(NO_3)_2O(ONO_2)(NCMe)]$	1·02	(I)	*i*
$[U(S_2CMe)_2O_2(OPPh_3)]$	1·02	(I)	*j*
$[U(S_2CNEt_2)_2O_2(ONMe_3)]$	1·03	(I)	*k*
$[U(S_2CNEt_2)_2O_2(OPPh_3)]$	1·03	(I)	*l*
$[U(S_2CNEt_2)_2O_2(OAsPh_3)]$	1·04	(I)	*l*
$[U(trop)_2O_2(py)]$	1·05	(I)	*m*
$[Nb(MeN{\cdot}CS{\cdot}Me)_2Cl_3]$	1·05	(I)	*n*
$[U(Se_2CNEt_2)_2O_2(OAsPh_3)]$	1·07	(I)	*o*
$[U(ox)_2O_2(Hox)]{\cdot}CHCl_3$	1·07	(I)	*p*
$[Nb(S_2CNEt_2)_2(OMe)_2Cl]$	1·11	(I)	*q*
$H_2[Nb(C_2O_4)_2O(OH)(OH_2)]{\cdot}4H_2O$	1·19	(I)	*r*
$[Mo\{C_6H_4(AsMe_2)_2\}_2Cl(CO)_2][I_3]{\cdot}2CHCl_3$	1·23	(II)	*s*
$[Ta\{(Me_2PCH_2)_2\}H(CO)_2]$	1·23	(II)	*t*
$[Re\{(Ph_2PCH_2)_2\}H_3]$	1·33	(II)	*u*

[a] py = Pyridine; quin = quinoline; trop = tropolonate; Hox = quinoline-8-ol. [c] R. Stomberg, *Arkiv. Kemi*, 1964, **22**, 49. [d] R. Stomberg, *Arkiv. Kemi*, 1965, **23**, 401. [e] J. M, LeCarpentier, R. Schlupp, and R. Weiss, *Acta Cryst.*, 1972, **B28**, 1278. [f] A. F. Cameron, D. W. Taylor, and R. H. Nuttall, *J.C.S. Dalton*, 1973, 2130. [g] A. F. Cameron, D. W. Taylor, and R. H. Nuttall, *J.C.S. Dalton*, 1972, 1608. [h] A. F. Cameron, D. W. Taylor, and R. H. Nuttall, *J.C.S. Dalton*, 1972, 1603. [i] F. W. B. Einstein, E. Enwall, D. M. Morris, and D. Sutton, *Inorg. Chem.*, 1971, **10**, 678. [j] G. Bombieri, U. Croatto, E. Forsellini, B. Zarli, and R. Graziani, *J.C.S. Dalton*, 1972, 560. [k] E. Forsellini, G. Bombieri, R. Graziani, and B. Zarli, *Inorg. Nuclear Chem. Letters*, 1972, **8**, 461. [l] R. Graziani, B. Zarli, A. Cassol, G. Bombieri, E. Forsellini, and E. Tondello, *Inorg. Chem.*, 1970, **9**, 2116. [m] G. Bombieri, S. Degetto, G. Marangoni, R. Graziani, and E. Forsellini, *Inorg. Nuclear Chem. Letters*, 1973, **9**, 233. [n] M. G. B. Drew and J. D. Wilkins, *J.C.S. Dalton*, 1974, 198. [o] B. Zarli, R. Graziani, E. Forsellini, U. Croatto, and G. Bombieri, *Chem. Comm.*, 1971, 1501; U. Croatto, *Atti Accad. Peloritana Pericolanti, Classe Sci. fis. mat. nat.*, 1971, **51**, 99. [p] D. Hall, A. D. Rae, and T. N. Waters, *Acta Cryst.*, 1967, **22**, 258. [q] J. W. Moncrief, D. C. Pantaleo, and N. E. Smith, *Inorg. Nuclear Chem. Letters*, 1971, **7**, 255. [r] N. Galesic, B. Matkovic, M. Herceg, and M. Sljukic, *J. Less-Common Metals*, 1971, **25**, 234, [s] M. G. B. Drew and J. D. Wilkins, *J.C.S. Dalton*, 1973, 2664, [t] The hydrogen atom was not located; P. Meakin, L. J. Guggenberger, F. N. Tebbe, and J. P. Jesson, *Inorg. Chem.*, 1974, **13**, 1025. [u] The hydrogen atoms were not located; V. G. Albano and P. L. Bellon, *J. Organometallic Chem.*, 1972, **37**, 151.

[4/2194 *Received, 25th October*, 1974]