Stereochemistry of Five-co-ordination. Part III.[1] Compounds of Stoicheiometry Bis (unidentate ligand) (tridentate ligand) metal

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Minimisation of the repulsive energy around five-co-ordinate molecules containing one tridentate and two unidentate ligands shows that neither the symmetrical trigonal bipyramid nor the square pyramid are the expected stereochemistries. For normal tridentate ligands, the predicted stereochemistry (I), contains a mirror plane through the central atom of the tridentate and both unidentate ligands, but the unidentate ligands are not symmetrically arranged on each side of the plane containing the three donor atoms of the tridentate ligand, and this tridentate plane does not contain the metal atom. A second stereochemistry, (II), is possible if the three donor atoms of the tridentate ligand form an equilateral triangle. These predictions agree with the crystal structures of molecules of this type.

A GOOD deal of structural work has recently been undertaken on the relatively large class of five-co-ordinate compounds [M(unidentate)$_2$(tridentate)]$^{x\pm}$. Probably the most significant finding is that the structures observed are very irregular, and do not correspond very closely to the trigonal bipyramid of C_{2v} symmetry, with unidentate ligands symmetrically above and below a plane containing the metal atom and the tridentate ligand, or to a regular square pyramid of C_s symmetry, where one unidentate ligand and three donor atoms of the tridentate ligand form a plane, with the other metal–unidentate ligand bond normal to this plane. For convenience of comparison with other five-co-ordinate molecules, the structure has usually been depicted as a grossly distorted trigonal bipyramid or square pyramid. This distortion is usually attributed to electronic factors, steric factors associated with the formation of chelate rings, and/or to intermolecular packing forces.

We have shown for the cases of co-ordination numbers five,[1] six,[2] seven,[3] and eight,[4] that introduction of bidentate ligands around the metal atom significantly alters the expected stereochemistries, and that these changes can be successfully predicted from a consideration of the repulsion between valence-shell electron pairs and/or ligands. To see if this approach could be extended to more complex polydentate ligands, a study of the relatively simple case of M(unidentate)$_2$(tridentate) was undertaken.

METHOD

The stereochemical arrangement of a number of ligand donor atoms surrounding a central metal atom may be calculated by minimisation of the total repulsion energy U, obtained by summing over all individual donor atom–donor atom repulsions (or alternatively the equivalent valence-shell electron-pair repulsions). It is assumed that the repulsive energy u_{ij} between any two donor atoms i and j (or alternatively, between any two electron pairs i and j) is proportional to some inverse power n of the distance d_{ij} between them. If all bond lengths are equal, that is all donor atoms lie on the surface of a sphere of radius r, then the results can be expressed in the form (1),

$$U = \Sigma_{ij}u_{ij} = \Sigma_{ij}ad_{ij}^{-n} = aXr^{-n} \qquad (1)$$

where a is the proportionality constant and X the repulsive-energy coefficient which is a function of n and the geometry of the co-ordination polyhedron. The most appropriate value of n cannot be known exactly, but certainly lies between the limits of 1 (for a purely Coulombic interaction) and 12.

The locations of the symmetrical tridentate ligand ABC and of each unidentate ligand D and E on the surface of the sphere are defined by their polar co-ordinates ϕ_i and θ_i, and the axes are defined by specifying that $\phi_A = \phi_B = \phi_C$, $\theta_B = 180°$, and $\theta_C = -\theta_A$ (Figure 1). The co-ordinates of the i atom are ϕ_i, which is defined as the angle between

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[1] Part II, D. L. Kepert, *Inorg. Chem.*, 1973, **12**, 1942.

[2] D. L. Kepert, *Inorg. Chem.*, 1972, **11**, 1561; *ibid.*, 1973, **12**, 1944.

[3] D. L. Kepert, *J.C.S. Dalton*, following paper.

[4] D. G. Blight and D. L. Kepert, *Inorg. Chem.*, 1972, **11**, 1556.

the M–i bond and the axis perpendicular to the ABC plane, and θ_i, which is defined as the angle between the plane vertical to ABC incorporating the M–i bond, and the plane vertical to ABC incorporating M and the midpoint of AC. The distance d_{ij} between any two such ligand sites i and j is given by (2).

$$d_{ij} = [2 - 2\cos\phi_i\cos\phi_j - 2\sin\phi_i\sin\phi_j\cos(\theta_i - \theta_j)]^{\frac{1}{2}}r \quad (2)$$

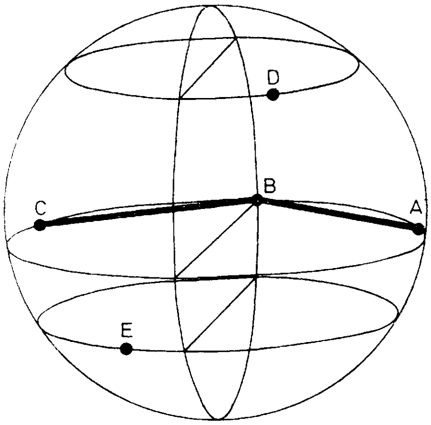


FIGURE 1 Generalised stereochemistry for M(unidentate)$_2$(tridentate) compounds

The geometry of the tridentate ligand is given by two variables. The 'normalised bite' b is defined as the distance between the two donor atoms of one arm of the tridentate ligand divided by the metal–ligand bond length [equation (3)]. The second variable is θ_A, which is equal

$$b = d_{AB}/r = d_{BC}/r \quad (3)$$

to the tridentate angle $\widehat{ABC}$.

It is assumed that each AB and BC arm of the tridentate ligand is sufficiently rigid that the interaction between its donor atoms can be considered to be constant, and can therefore be neglected when comparing otherwise different stereochemistries. Two limiting assumptions can be made about the rigidity of the tridentate ligand with respect to the tridentate angle θ_A and the interaction between A and C. (*i*) The tridentate ligand is completely flexible: the two arms of the ligand are freely hinged at B, and repulsion between A and C is included in the total-energy function. (*ii*) The tridentate ligand is completely rigid: the tridentate angle is fixed, and hence u_{AC} is constant and may be omitted from the total-energy function. In this case ϕ_A is also fixed for any given value of b, and is given by: $\phi_A = \arcsin[b/2\cos(\theta_A/2)]$. The ligand–ligand repulsion energy was calculated as a function of ϕ_A, θ_A, ϕ_D, θ_D, ϕ_E, and θ_E, using each of these two limiting assumptions. The location of each minimum on the potential-energy surface was determined to the nearest 0·1° in each of the angular co-ordinates.

RESULTS

Flexible Tridentate.—The stereochemistry corresponding to the single minimum on the potential-energy surface was always found to contain a mirror plane including the unidentate ligands D and E, that is $\theta_D = \theta_E = 0°$. The remaining four co-ordinates calculated for $n = 1$, 6, and 12 are shown as a function of normalised bite b in Figure 2. In all cases $\phi_E > \phi_A > \phi_D$, that is the unidentate ligands lie on opposite sides of the tridentate plane. It can be seen however, that the co-ordinates vary in a remarkably irregular and unexpected manner with changing normalised bite.

The minima on the potential-energy surfaces were fairly shallow, particularly with regard to variation in ϕ_D and ϕ_E in the range b = 1·2 to *ca.* 1·35. That is, introduction of the tridentate ligand around the five-co-ordinate metal atom does not necessarily lead to a more rigid structure. However, the angle $\widehat{DME} = \phi_E - \phi_D$ between the two metal–unidentate ligand bonds varied with normalised bite in a much more regular manner (Figure 3), being in the range of 100—110° for $b < 1·4$, and then increasing steeply with increasing b.

The two most important stereochemical predictions from Figure 2 are as follows. (*i*) Regardless of the value of the normalised bite, ϕ_A is never equal to 90°, and ϕ_D is never equal to 180° − ϕ_E. That is, in no case is the structure that of a C_{2v} trigonal bipyramid with the tridentate ligand lying on a mirror plane, although this would have intuitively appeared to be a reasonable structure.

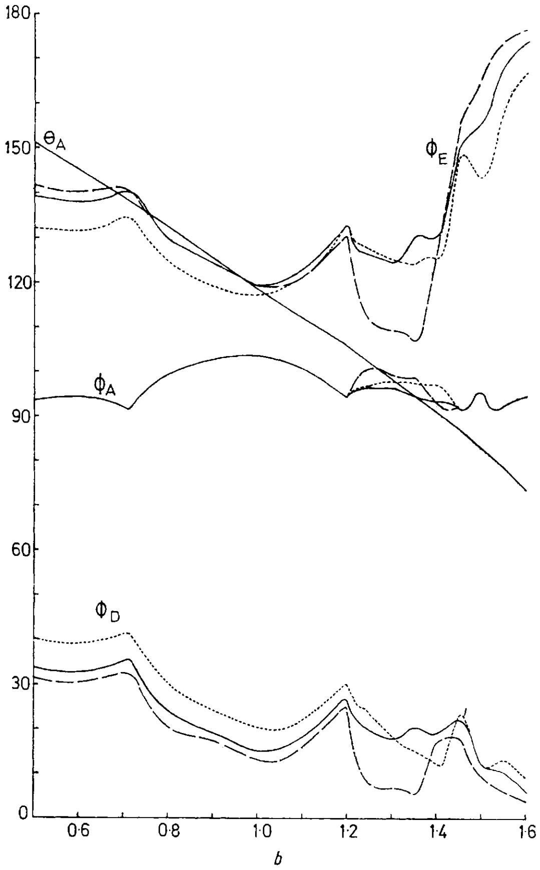


FIGURE 2 Angular co-ordinates (°) for M(unidentate)$_2$(flexible tridentate) compounds [structure (I)] as a function of normalised bite b: (· · · ·), $n = 1$; (——), $n = 6$; (— — —), $n = 12$

(*ii*) Again regardless of the value of the normalised bite, ϕ_E is never equal to ϕ_A, and ϕ_D is never equal to 0°. That is, the structure never becomes that of a square pyramid, even for those cases where $\theta_A = 90°$ (at b *ca.* 1·4).

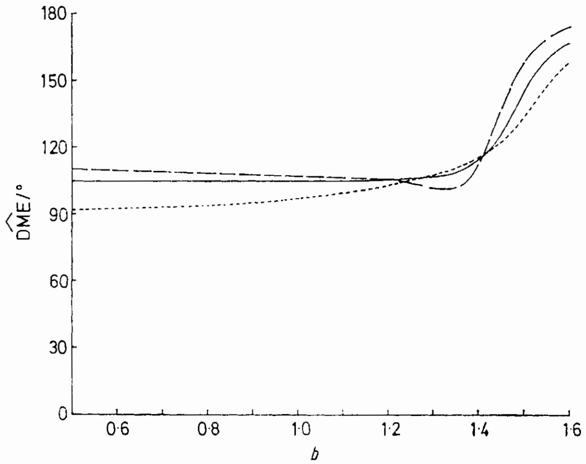


FIGURE 3 Bond angle DME (°) for M(unidentate)$_2$(flexible tridentate) compounds [structure (I)] as a function of normalised bite b: (· · · ·) $n = 1$; (——), $n = 6$; (— — —), $n = 12$

Rigid Tridentate.—Values of ϕ_D and ϕ_E for the minima on the potential-energy surfaces for M(unidentate)$_2$(rigid tridentate) are shown in Figure 4 as a function of b and θ_A for $n = 6$. The curves for $n = 1$ and 12 are very similar. (It should be noted that if the value of θ_A used for the rigid-tridentate-ligand calculations is fortuitously the same as that obtained from the flexible-tridentate-ligand calculations for the same value of b, then the same values of ϕ_D and ϕ_E will be obtained with both limiting assumptions.) The C_{2v} trigonal bipyramid can only occur for the particular cases where $\phi_A \equiv 90°$, which is when θ_A and b are related by $\theta_A = 2\arccos(b/2)$. In this case, D and E are symmetrically each side of the tridentate ligand.

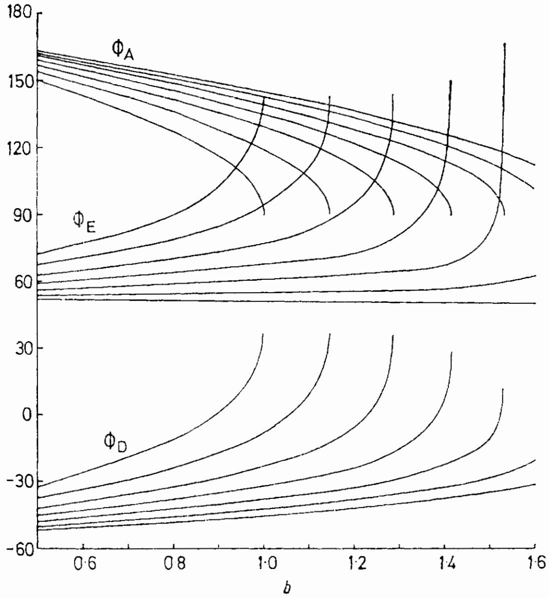
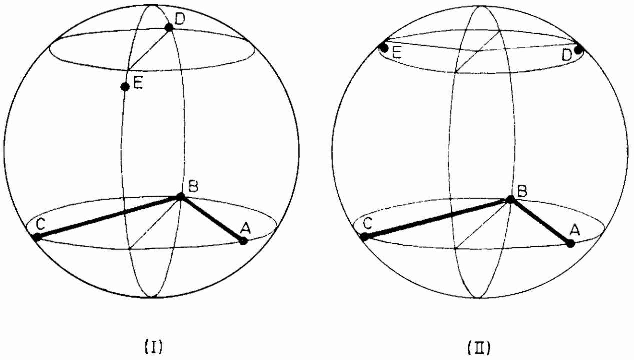


FIGURE 4 Angular co-ordinates (°) for M(unidentate)$_2$(rigid tridentate) compounds [structure (I)] as a function of normalised bite b for $n = 6$

For any value of θ_A, an increase of ϕ_A above 90° decreased both ϕ_D and ϕ_E. In contrast to the limiting case of the flexible tridentate ligand, ϕ_E can become less than ϕ_A at low values of b and/or θ_A, with both unidentate ligands lying on the same side of the tridentate ligand. As the normalised bite approached zero, ϕ_E approached $-\phi_D$. (For the sake of continuity, the position of the unidentate ligand D in Figure 4 is given as negative values of ϕ_D maintaining $\theta_D = 0$, rather than the alternative of maintaining positive values of ϕ_D but with $\theta_D = 180°$.) A square pyramid will be formed only if the passing of ϕ_E across the ϕ_A ϕ_B ϕ_C plane coincides with ϕ_D passing through 0°. This occurred only for the case of $\theta_A \equiv 90{\cdot}0$: and b *ca.* 1·38 (b = 1·37, 1·38, and 1·40 for n = 1, 6, and 12 respectively).



(I) (II)

FIGURE 5 Relation between structures (I) and (II) for $\theta_A = 60°$, $b = 1{\cdot}2$, and $n = 6$

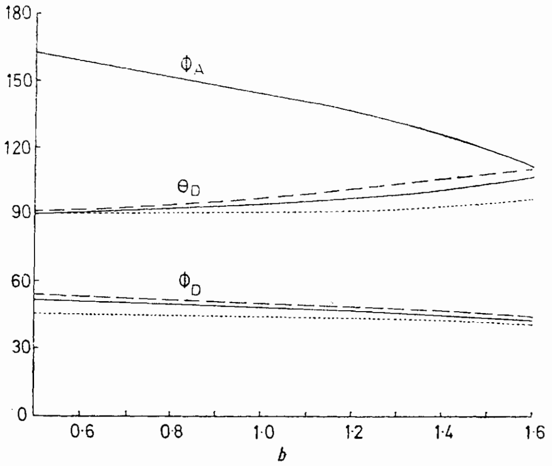


FIGURE 6 Angular co-ordinates (°) for M(unidentate)$_2$(rigid tridentate) compounds [structure (II)] as a function of normalised bite b: (· · · ·), $n = 1$; (——), $n = 6$; (— — —), $n = 12$

For the particular case of $\theta_A = 60°$, ABC is an equilateral triangle and the minima on the potential-energy surfaces were more difficult to precisely locate as a long trough was formed which corresponds to rotation of D and E from the above stereochemistry having $\theta_D = \theta_E = 0°$, (I), to a stereochemistry having $\phi_{\mathrm{D}} = \phi_{\mathrm{E}}$ and $\theta_{\mathrm{E}} = -\theta_{\mathrm{D}}$, (II), (Figure 5). There are three equivalent orientations of structure (I) depending on which triangular ABC edge is at right angles to the projection of DE, and also three equivalent orientations of structure (II) depending on which triangular edge is parallel to the projection of DE. Which of these two structures is the most stable depends on the values of n and b. The energy of both structures for all values of n, b, and θ_{A} is best obtained by artificially imposing a mirror plane through $\theta = 0°$. The resultant angular parameters of the potential-energy minima for structures (I) and (II) are shown in Figures 4 and 6, respectively. The ligand–ligand repulsion energy of structure (II) relative to that of (I) (Table 1) shows that the energy difference is not significant, and corresponds to free rotation of DE about the axis normal to the tridentate plane (previous experience[1–4] suggests that energy ratios of less than *ca.* 1·001, *ca.* 1·01, and *ca.* 1·1 : 1 for n = 1, 6, and 12, respectively, are not significant). Structure (II) does not occur as a minimum for higher values of θ_{A}, and even if this structure is enforced by imposing the conditions that $\phi_{\mathrm{D}} = \phi_{\mathrm{E}}$ and $\theta_{\mathrm{E}} = -\theta_{\mathrm{D}}$, the ligand–ligand repulsion energy is clearly unfavourable for $\theta_{\mathrm{A}} = 70°$ (Table 1), or higher values of θ_{A}.

TABLE 1

Ligand–ligand repulsion energy for structure (II) relative to structure (I) [X(II)/X(I)]

	$\theta_{\mathrm{A}} = 60°$			$\theta_{\mathrm{A}} = 70°$		
b	$n = 1$	$n = 6$	$n = 12$	$n = 1$	$n = 6$	$n = 12$
0·5	1·0000	1·000	1·00	1·0010	1·022	1·07
0·6	1·0000	1·000	1·00	1·0015	1·030	1·11
0·7	1·0000	1·000	1·00	1·0021	1·042	1·14
0·8	1·0000	1·000	1·00	1·0029	1·057	1·19
0·9	1·0000	1·001	1·00	1·0039	1·074	1·24
1·0	1·0000	1·000	1·00	1·0051	1·095	1·30
1·1	1·0000	1·000	1·00	1·0067	1·120	1·37
1·2	1·0000	1·000	1·00	1·0088	1·150	1·46
1·3	1·0000	0·999	0·99	1·0116	1·187	1·56
1·4	1·0001	0·998	0·98	1·0156	1·237	1·68
1·5	1·0001	0·996	0·96	1·0223	1·307	1·86
1·6	1·0003	0·991	0·94	1·0392	1·450	2·22

DISCUSSION

The results of these calculations, using either of the two limiting assumptions, show that the expected stereochemistries are not the same as may have been expected by analogy with the stereochemistry of complexes containing only unidentate ligands. This conclusion arises simply from the relative rigidity of the chelate rings, and is quite distinct from any other steric interactions in the molecule. Thus care is needed in describing the stereochemistry of complexes containing multidentate ligands.

Those molecules of the type [M(unidentate)$_2$(tridentate)]$^{x\pm}$ whose structure is known are listed in Table 2. Tridentate ligands which may be symmetrical about the central donor atom are listed separately to unsymmetrical ligands, as the two different arms of the latter may have different normalised bites and different metal–ligand bond lengths.

TABLE 2

Structural parameters for compounds [M(unidentate)$_2$(tridentate)]

	b	R[a]	θ_{A}	ϕ_{A}	ϕ_{D}	ϕ_{E}	DME	Ref.
Structure (I)								
Symmetric tridentate ligands								
CoCl$_2${MeN(CH$_2$CH$_2$NMe$_2$)$_2$}	1·22, 1·24	0·94, 0·93	89	111	−16	87	104	*b*
	1·22, 1·23	0·90, 0·92	87	110	−16	88	104	*b*
ZnCl$_2$(terpy) [c]	1·22, 1·25	1·04, 1·07	101	116	27	139	112	*d*
CoCl$_2$(terpy) [c]	1·23, 1·24	1·04, 1·02	102	110	−11	100	111	*e*
Co(NCS)$_2${(C$_3$H$_7$S)N(CH$_2$CH$_2$NEt$_2$)$_2$}	1·27, 1·27	0·96, 0·96	88	113	−22	78	99	*f*
NiBr$_2${HN(CH$_2$·C$_5$H$_3$N·Me)$_2$}	1·32, 1·33	1·02, 1·02	96	103	9	158	149	*g*
Ni(NCS)$_2${(C$_{14}$H$_{14}$As)N(CH$_2$CH$_2$NEt$_2$)$_2$}	1·35, 1·37	1·05, 1·07	93	113	−15	86	100	*h*
NiBr$_2${HN(CH$_2$CH$_2$PPh$_2$)$_2$}	1·42, 1·42		89	114	−25	76	101	*i*
NiBr$_2${MeAs(CH$_2$CH$_2$CH$_2$AsMe$_2$)$_2$}	1·41, 1·43	1·00, 1·00	89	93	2	113	111	*j*
CoCl$_2${HN(CH$_2$CH$_2$NEt$_2$)$_2$}	(1·30, 1·30)	(1·01, 1·02)	(84)	(121)	(−38)	(65)	(102)	*k*
CuBr(N$_3$){HN(CH$_2$CH$_2$NEt$_2$)$_2$}	1·38, 1·41	1·07, 1·10	81	124	−34	65	99	*l*
Asymmetric tridentate ligands								
CoCl$_2$(C$_5$H$_4$N·CH⁚N·NH·C$_5$H$_4$N)	1·21, 1·22	1·03, 1·02					110	*m*
ZnBr$_2$(C$_5$H$_4$N·CH⁚N·CH$_2$CH$_2$NMe$_2$)	1·22, 1·24	1·08, 1·07					114	*n*
Co(NCS)$_2${Et$_2$NCH$_2$CH$_2$NHCH$_2$CH$_2$P(O)Ph$_2$	1·26, 1·36	0·95					98	*o*
NiBr$_2$(MeOC$_6$H$_4$CH$_2$NHCH$_2$CH$_2$CH$_2$NHEt)	1·39, 1·50	1·00					150	*p*
Structure (II)								
CuCl$_2${S(CH$_2$·CO·NMe$_2$)$_2$}	1·22, 1·23	0·84, 0·95	63					*q*

[a] The bond lengths to the tridentate ligand are not always exactly equal, and the bond-length ratio R is defined by $R = d(\mathrm{M{-}A})/d(\mathrm{M{-}B}) = d(\mathrm{M{-}C})/d(\mathrm{M{-}B})$. This ratio is only given when the donor atoms are of the same element. [b] Two independent molecules in the unit cell. M. Di Vaira and P. L. Orioli, *Inorg. Chem.*, 1969, **8**, 2729. [c] terpy = 2,2′,2″-Terpyridine. [d] D. E. C. Corbridge and E. G. Cox, *J. Chem. Soc.*, 1956, 594. W. B. Einstein and B. R. Penfold, *Acta Cryst.*, 1966, **20**, 924. [e] E. Goldschmied and N. C. Stephenson, *Acta Cryst.*, 1970, **B26**, 1867. [f] P. Dapporto and M. Di Vaira, *J. Chem. Soc.* (*A*), 1971, 1891. [g] J. Rogers and R. A. Jacobson, *J. Chem. Soc.* (*A*), 1970, 1826. [h] M. Di Vaira, *J. Chem. Soc.* (*A*), 1971, 148. [i] P. L. Orioli and C. A. Ghilardi, *J. Chem. Soc.* (*A*), 1970, 1511. [j] G. A. Mair, H. M. Powell, and D. E. Henn, *Proc. Chem. Soc.*, 1960, 415. [k] Z. Dori, R. Eisenberg, and H. B. Gray, *Inorg. Chem.*, 1967, **6**, 483. [l] R. F. Ziolo, M. Allen, D. D. Titus, H. B. Gray, and Z. Dori, *Inorg. Chem.*, 1972, **11**, 3044. [m] M. Gerloch, *J. Chem. Soc.* (*A*), 1966, 1317. [n] G. Zakrzewski and E. C. Lingafetter, *Inorg. Chim. Acta*, 1970, **4**, 251. [o] C. A. Ghilardi and A. B. Orlandini, *J.C.S. Dalton*, 1972, 1698. [p] R. L. Orioli and M. Di Vaira, *J. Chem. Soc.* (*A*), 1968, 2078. [q] J. Coetzer, *Acta Cryst.*, 1970, **B26**, 1414.

The first eight compounds listed in Table 2, with symmetrical tridentate ligands and with the same unidentate ligands, are clearly of structure (I). [The next compound, $CoCl_2\{HN(CH_2CH_2NEt_2)_2\}$, is similar but slightly twisted, the sum of the angles $\widehat{BMD}$, $\widehat{DME}$, and $\widehat{BME}$ being only 358·5°, instead of the expected 360·0°. Examination of the structure clearly shows that the chlorine atom at site D is pushed out of the mirror plane by one of the ethyl groups on the nitrogen atom at site C. An alternative way of relieving this steric strain would be to decrease both ϕ_D and ϕ_E, but this would increase further the considerable steric interaction between the chlorine atom at site E and the ethyl groups. These unusual carbon–chlorine interactions are discussed in more detail by Dori *et al.*[5]] For these compounds of structure (I), the observed ϕ_A value is always greater than 90° as predicted. The observed ranges of ϕ_A (93—116°) and θ_A (87—102°) may be compared with the ranges of ϕ_A (91—111°) and θ_A (89—104°) predicted for the limiting case of the flexible tridentate ligand over this fairly narrow range of normalised bite.

That the tridentate ligands are moderately flexible, at least over small ranges of θ_A, is also indicated by the two 2,2′,2″-terpyridyl complexes for which $\theta_A = 101$ and 102°. This may be compared with 120° for the free ligand, showing that the two arms of the tridentate ligand are considerably drawn towards each other by the metal atom. The other tridentate ligands in Table 2 contain aliphatic chains linking the donor atoms, and would be expected to be even more flexible.

Although it is not possible to predict the values of ϕ_D or ϕ_E, it is possible to predict the difference between them, which is the angle $\widehat{DME}$ between the two metal–unidentate ligand bonds. Provided *b* is below 1·4, the predicted value of $\widehat{DME}$ is 100—110° (Figure 3) This agrees very well for all but one of the compounds containing symmetrical tridentate ligands listed in Table 2. The notable exception is the compound $NiBr_2\{HN(CH_2{\cdot}C_5H_3N{\cdot}Me)_2\}$ for which the Br–Ni–Br angle is very much greater at 149°, but the deviation can be attributed to fairly obvious steric factors. This chelate ligand contains bulky methyl groups attached to the pyridine rings, and these project towards each other in the plane of the tridentate forcing the two bromine atoms further apart. The only other related symmetrical tridentate ligand is 2,2′,2″-terpyridyl in which these sites are occupied by hydrogen atoms, which do not appear to exert any perceptible steric effect. In all other cases the terminal donor atoms of the tridentate ligands are tetrahedrally co-ordinated, and there are no steric interactions of this type. The large Br–Ni–Br angle observed with the asymmetric $MeOC_6H_4CH_2NHCH_2CH_2CH_2NHEt$ is similarly readily attributed to the methoxy-group projecting between the bromine atoms.

The only compound whose value of θ_A is markedly different to that predicted for the limiting flexible tridentate ligand (90—100°) is $CuCl_2\{S(CH_2{\cdot}CO{\cdot}NMe_2)_2\}$, for which $\theta_A = 63°$. Models clearly show that such ligands with bulky donor atoms at the hingeing B site, and which form five-membered chelate rings, cannot behave as tridentate ligands with large values of θ_A. This is the only known compound having structure (II). The two chlorine atoms are projected over the O–O edge and one S–O edge of the OSO triangle of donor atoms.

The only other compounds relevant to this work are $[Cu(H_2O)_2\{O_2CC(Me)NCH_2CH_2CO_2\}],2H_2O$ [6] and $NiI_2\{PhP(C_6H_4SMe)_2\}$.[7] The former is intermediate between structure (I) and a four-co-ordinate square-planar complex, one $Cu-OH_2$ distance (2·41 Å) being much longer than the other (1·95 Å). In the second case the large hingeing phosphorus atom and the two five-membered chelate rings again force a small tridentate angle ($\theta_A = 64°$), and the stereochemistry is best considered as being intermediate between structure (II) and a four-co-ordinate square-planar complex, one Ni–S distance (2·79 Å) being much longer than the other (2·19 Å).

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