

Table I. Angular Parameters and Ligand-Ligand Repulsion Coefficients for $M(\text{bidentate})_2(\text{monodentate})$

	Irregular trigonal bipyramid			Rectangular pyramid		
	$n = 1$	$n = 6$	$n = 12$	$n = 1$	$n = 6$	$n = 12$
$b = 1.0$	ϕ_A^b	a	a	108.0	109.4	109.5
	ϕ_B			108.0	109.5	109.5
	X			4.7597	0.3753	0.0193
$b = 1.1$	ϕ_A	a	a	107.2	107.8	107.4
	ϕ_B			107.2	107.8	107.4
	X			4.8119	0.4083	0.0235
$b = 1.2$	ϕ_A	a	a	106.2	105.8	104.9
	ϕ_B			106.2	105.9	104.9
	X			4.8761	0.4546	0.0302
$b = 1.3$	ϕ_A	97.5	99.0	105.0	103.6	102.0
	ϕ_B	113.4	109.2	105.0	103.6	102.0
	X	4.9549	0.5217	4.9558	0.5219	0.0418
$b = 1.4$	ϕ_A	90.8	90.8	103.7	101.0	98.8
	ϕ_B	119.3	119.1	103.7	101.0	98.8
	X	5.0464	0.6119	5.0568	0.6252	0.0640
$b = 1.5$	ϕ_A	85.7	85.9	102.0	98.0	95.3
	ϕ_B	123.6	124.6	102.0	98.0	95.3
	X	5.1517	0.7292	5.1884	0.7988	0.1157

^a Does not occur as a minimum on the potential energy surface.
^b ϕ values in degrees.

Table II. Structural Parameters for $M(\text{bidentate})_2(\text{monodentate})^a$

	b	ϕ_A , deg	ϕ_B , deg	Ref
$[\text{As}^{\text{III}}(\text{S}_2\text{CNEt}_2)_2(\text{Ph})]$	1.12	93.9	94.4	<i>b</i>
$[\text{Zn}^{\text{II}}(\text{S}_2\text{CNMe}_2)_2(\text{C}_6\text{H}_5\text{N})] \cdot 0.5\text{C}_6\text{H}_6$	1.19	94.9	116.5	<i>c</i>
$[\text{Fe}(\text{S}_2\text{CNMe}_2)_2(\text{NO})]$	1.23	105.7	105.9	<i>d</i>
$[\text{Fe}^{\text{III}}(\text{S}_2\text{CNEt}_2)_2\text{I}]$	1.23	101.3	108.8	<i>e</i>
$[\text{Fe}^{\text{III}}(\text{S}_2\text{CNEt}_2)_2\text{Cl}]$	1.24	105.5	105.9	<i>f</i>
$[\text{Co}(\text{S}_2\text{CNMe}_2)_2(\text{NO})]$	1.24	102.9	103.6	<i>g</i>
$[\text{Cu}^{\text{II}}(\text{bipy})_2(\text{NH}_3)(\text{BF}_4)_2]$	1.28	92.2	125.9	<i>h</i>
$[\text{Cu}^{\text{II}}(\text{MeCHOHCOO})_2(\text{H}_2\text{O})] \cdot 0.5\text{C}_6\text{H}_6$	1.31	92.7	95.9	<i>i</i>
$[\text{Cu}^{\text{II}}(\text{bipy})_2\text{I}]\text{I}$	1.31	90.5	123.0	<i>j</i>
$\text{Na}(\text{Et}_4\text{N})[\text{V}^{\text{VO}}(\text{Ph}_2\text{COCO}_2)_2] \cdot 2\text{PrOH}$	1.31	104.2	113.6	<i>k</i>
$[\text{V}^{\text{VO}}(\text{MeCOCHCOMe})_2]$	1.38	105.2	107.3	<i>l, m</i>
$[\text{V}^{\text{VO}}(\text{PhCOCHCOMe})_2]$	1.38	105.0	106.6	<i>m, n</i>
$[\text{Zn}^{\text{II}}(\text{MeCOCHCOMe})_2(\text{H}_2\text{O})]$	1.39	98.9	104.9	<i>o</i>
$[\text{Zn}^{\text{II}}(\text{PhCOCHCOMe})_2(\text{EtOH})]$	1.41	97.2	101.5	<i>p</i>
$[\text{Cu}^{\text{II}}(\text{MeCOC}_6\text{H}_4\text{O})_2(\text{MeC}_6\text{H}_4\text{N})]$	1.43	94.4	101.1	<i>q</i>
$[\text{Cu}^{\text{II}}(\text{PhN}=\text{CC}_6\text{H}_4\text{O})_2(\text{C}_6\text{H}_5\text{N})]$	1.43	95.3	96.9	<i>r</i>

^a Restricted to compounds which have at least an approximate twofold axis. ^b R. Bally, *Acta Crystallogr.*, **23**, 295 (1967).
^c K. A. Fraser and M. M. Harding, *ibid.*, **22**, 75 (1967). ^d G. R. Davies, J. A. J. Jarvis, B. T. Kilbourne, R. H. B. Mais, and P. G. Owston, *J. Chem. Soc. A*, 1275 (1970). ^e P. C. Healy, A. H. White, and B. F. Hoskins, *J. Chem. Soc., Dalton Trans.*, 1369 (1972).
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shallow minima are very dependent upon the value of n . These minima progressively deepen and move further apart as the normalized bite is further increased ($b = 1.5$, Figure 4).

Detailed angular parameters for these minima for n values of 1, 6, and 12 and over a larger range of normalized bite

are illustrated in Figure 5 and, including the ligand-ligand repulsion coefficients, in Table I. Removal of the restrictions imposed by the assumed C_2 axis showed that each of these minima were true minima. Although the single minimum at small bites corresponding to the rectangular pyramid is replaced by the two minima at large bites due to the irregular trigonal bipyramids, the rectangular pyramid can still be located as the saddle separating these minima. This extension is shown by the broken lines in Figure 5. The curves for different values of n cross at $b = 2^{1/2} = 1.414$ and $\phi = 90.0$ and 120.0° corresponding to the regular trigonal bipyramid.

Those compounds which have been structurally characterized (Table II) have normalized bites below 1.4 where the potential energy surfaces are at least as flat as those observed for $M(\text{monodentate})_5$.³ As expected the observed stereochemistry again ranges from trigonal bipyramidal to rectangular pyramidal. The apparent concentration of structures near the rectangular pyramid is partly due to the stabilization of this structure relative to the irregular trigonal bipyramid, but is also at least partly due to the inclusion of vanadyl complexes and copper complexes in Table II. In VO^{2+} complexes the single, short vanadium-oxygen bond stabilizes the pyramidal structure with relatively high values of ϕ_A and ϕ_B . Some of the copper(II) complexes can alternatively be regarded as being square planar with one additional weak bond normal to the plane and have relatively low values of ϕ_A and ϕ_B . The poor agreement between calculated and observed stereochemistry for $[\text{As}^{\text{III}}(\text{S}_2\text{CNEt}_2)_2(\text{Ph})]$ can be attributed to the very asymmetric chelate rings (As-S bond lengths of 2.33 and 2.87 Å to each chelate) and/or to the steric effect of the lone pair on the arsenic(III).

Acknowledgments. This work was carried out while on leave at the University Chemical Laboratories, University of Cambridge, and thanks are due to Professor J. Lewis and his colleagues for their hospitality.

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Stereochemistry of Six-Coordinate $M(\text{bidentate})_2(\text{monodentate})_2$

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Received October 31, 1972

The relative stability of different isomers and also their detailed stereochemistry resulting from the introduction of bidentate ligands into the coordination sphere can be determined with remarkable accuracy and simplicity by calculating the total ligand-ligand repulsion energy. The previous investigations into five-,¹ six-,² and eight-coordinate³ complexes of the types $M(\text{bidentate})_2(\text{monodentate})$, $M(\text{bidentate})_3$, $M(\text{bidentate})_2(\text{monodentate})_4$, and $M(\text{bidentate})_4$ is now extended to the six-coordinate $M(\text{bidentate})_2(\text{monodentate})_2$.

- (1) D. L. Kepert, *Inorg. Chem.*, **12**, 1942 (1973).
- (2) D. L. Kepert, *Inorg. Chem.*, **11**, 1561 (1972).
- (3) D. G. Blight and D. L. Kepert, *Inorg. Chem.*, **11**, 1556 (1972).

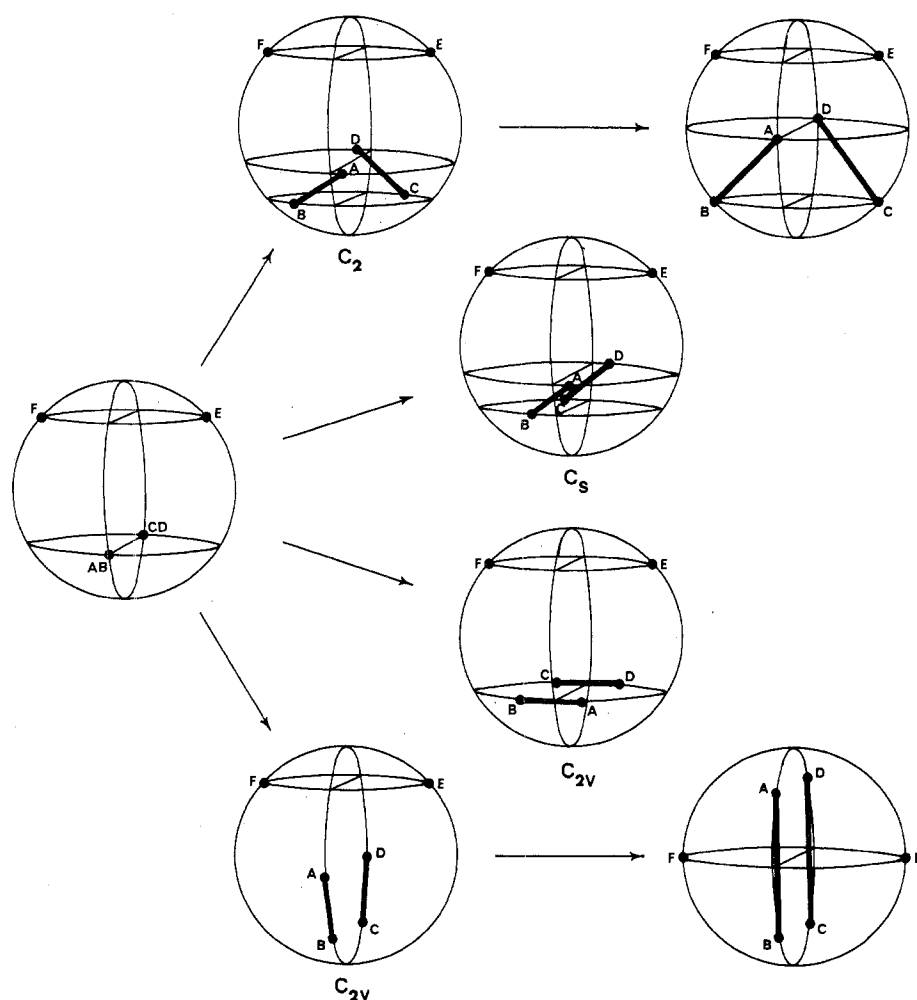


Figure 1. The generation of different isomers of $M(\text{bidentate})_2(\text{monodentate})_2$ as the ligand bite is increased from zero.

Method

The most convenient way to imagine the generation of different isomers of $M(\text{bidentate})_2(\text{monodentate})_2$ is to start with the bidentates having zero "bite." The two monodentates E and F and the two coalesced bidentates AB and CD are then arranged at the corners of a tetrahedron (Figure 1).

Four different structures may be envisaged as being created as the "bite" of the bidentate ligands is progressively increased (Figure 1). First, retention of the twofold axis leads to an irregular polyhedron of C_2 symmetry and ultimately to the cis octahedral structure. Second, retention of the mirror plane leads to the irregular polyhedron of C_s symmetry, which for convenience will be referred to as the distorted pentagonal pyramid, the atoms ABCDE being considered to form the distorted pentagonal plane. The third and fourth isomers are formed by retention of both the twofold axis and the mirror plane and have C_{2v} symmetry. The trigonal prism is formed if the bidentates remain parallel to the EF edge. Alternatively if the plane containing the bidentates remains normal to the EF edge, a skew trapezoidal bipyramid is formed, which becomes the usual trans octahedral structure as the bite is further increased (Figure 1).

Each ligand site is defined by the spherical coordinates ϕ and θ . The coordinate ϕ is defined as the angle between the metal-ligand bond and the axis passing through the metal atom and bisecting the EF edge. The "longitude" θ is defined as the angle between the vertical plane normal to the EF edge passing through the metal atom and the vertical plane incorporating the metal-ligand bond.

Table I. Spherical Coordinates (in Degrees)

Cis octahedral		Distorted pentagonal pyramid		Trigonal prism		Skew trapezoidal bipyramid		
	θ	ϕ	θ	ϕ	θ	ϕ	θ	
A	ϕ_A	θ_A	ϕ_A	θ_A	ϕ_A	θ_A	ϕ_A	0
B	ϕ_B	θ_B	ϕ_B	θ_B	ϕ_A	$-\theta_A$	ϕ_B	0
C	ϕ_B	$180 + \theta_B$	ϕ_B	$180 - \theta_B$	ϕ_A	$180 + \theta_A$	ϕ_B	180
D	ϕ_A	$180 + \theta_A$	ϕ_A	$180 - \theta_A$	ϕ_A	$180 - \theta_A$	ϕ_A	180
E	ϕ_E	90	ϕ_E	90	ϕ_E	90	ϕ_E	90
F	ϕ_E	270	ϕ_E	270	ϕ_E	270	ϕ_E	270

All six ligand sites are defined for each stereochemistry by the five variables ϕ_A , θ_A , ϕ_B , θ_B , and ϕ_E in Table I.

The distance d_{ij} between any two such ligand sites i and j is given by

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

where r is the metal-ligand distance. One of the four variables ϕ_A , θ_A , ϕ_B , and θ_B can therefore be calculated from the other three and the "normalized bite" b , which is defined as the distance between the two donor atoms of the chelate divided by the metal-ligand bond length

$$b = d_{AB}/r = d_{CD}/r$$

It is again assumed that the repulsive energy u_{ij} between any two donor atoms is inversely proportional to the n th power of the distance between them. The total ligand-ligand repulsion energy is obtained from

$$U = \sum u_{ij} = aXr^{-n}$$

The ligand-ligand repulsion energy coefficient X is a direct measure of the relative energy of the particular stereochemistry.

The chelated ligand is again assumed to be sufficiently rigid that the interaction between its two donor atoms can be regarded as constant.

The total ligand-ligand repulsion energy for each stereochemistry was calculated as a function of ϕ_A , θ_A , θ_B , and ϕ_E for each selected value of the normalized bite, and the location of the minimum on the appropriate potential energy surface was determined to the nearest 0.1° in each of the angular coordinates.

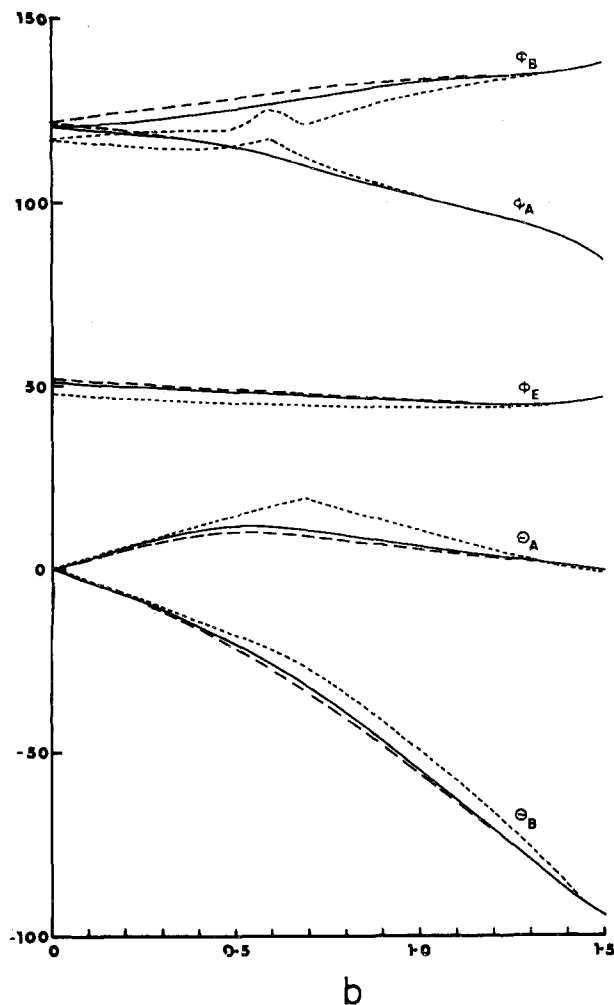


Figure 2. Angular parameters in degrees for cis octahedral $M(\text{bidentate})_2(\text{monodentate})_2$ as a function of normalized ligand bite, b : dotted line, $n = 1$; full line, $n = 6$; broken line, $n = 12$.

Results

The angular coordinates corresponding to the minimum on each potential energy surface (within the limits imposed by the assumed symmetry in each case) are shown for each stereochemistry in Figures 2-5 for values of n of 1, 6, and 12. (It may be noted that the tetrahedron corresponding to zero bite is not regular with $\phi_A = 125.3^\circ$ and $\phi_E = 54.7^\circ$ since the repulsion from *both* "ends" of the coalesced bidentate is counted in the total repulsive energy).

The values for the repulsive energy coefficients X for all four stereochemistries are shown in Figure 6 normalized to those of the skew trapezoidal bipyramid-trans octahedral

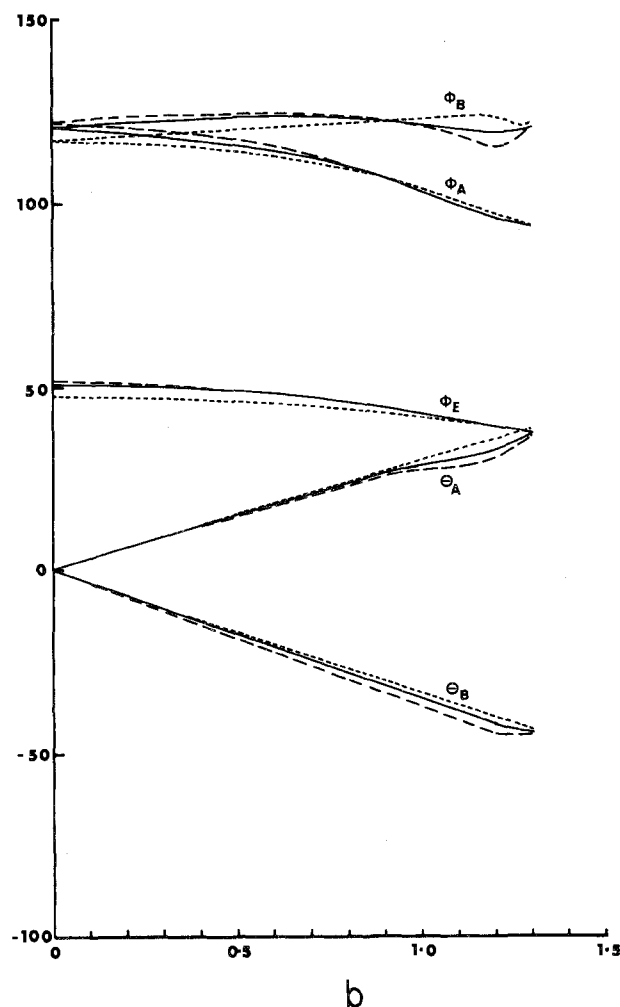


Figure 3. Angular parameters in degrees for pentagonal-pyramidal $M(\text{bidentate})_2(\text{monodentate})_2$ as a function of normalized ligand bite, b : dotted line, $n = 1$; full line, $n = 6$; broken line, $n = 12$.

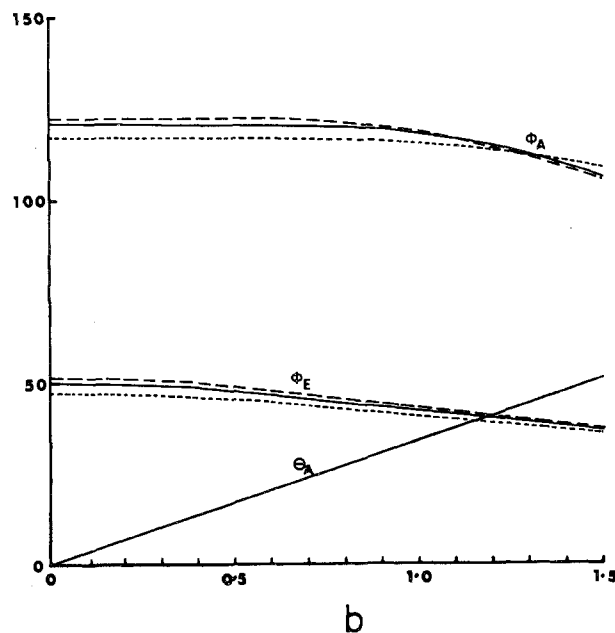


Figure 4. Angular parameters in degrees for trigonal-prismatic $M(\text{bidentate})_2(\text{monodentate})_2$ as a function of normalized ligand bite, b : dotted line, $n = 1$; full line, $n = 6$; broken line, $n = 12$.

structure which are equated to unity. The skew trapezoidal

Table II. Stereochemistry of M(bidentate)₂(monodentate)₂^a

	<i>b</i>	Structure	Ref		<i>b</i>	Structure	Ref
[Cr(O ₂) ₂ O(py)]	0.773	Pent pyr	<i>b</i>	[Pt(en) ₂ Cl ₂]Cl ₂	1.337	Cis	<i>ii</i>
(NH ₄) ₃ [(V(O ₂) ₂ O) ₂ O]	0.773	Pent pyr	<i>c</i>	[Ni(NH ₂ CSNHNH ₂) ₂ (H ₂ O) ₂]	1.338	Trans	<i>jj</i>
(NH ₄) ₃ [V(O ₂) ₂ O(NH ₃)]	0.781	Peny pyr	<i>d</i>	[Ni(NH ₂ CSNHNH ₂) ₂ (SCN) ₂]	1.342	Trans	<i>kk</i>
[Co(NO ₃) ₂ (Me ₃ PO) ₂]	0.957	Cis	<i>e</i>	[Ni(dimeen) ₂ (ONO) ₂]	1.342	Trans	<i>ll</i>
[Hg(<i>o</i> -phen) ₂ (SCN) ₂]	1.111	Cis	<i>f</i>	[Ni(en) ₂ Cl(NCS)]	1.345	Cis	<i>mm</i>
[Sn(S ₂ CNEt ₂) ₂ (SCSN ₂ Et ₂) ₂]	1.156	Cis	<i>g</i>	[Ni(dimeen) ₂ Br ₂]	1.347	Trans	<i>nn</i>
[Ru(S ₂ CNEt ₂) ₂ (SCSN ₂ Et ₂)(NO)]	1.19	Cis	<i>h</i>	[Cr(en) ₂ Cl ₂]Cl·HCl·2H ₂ O	1.354	Trans	<i>oo</i>
[Sn(oxine) ₂ Me ₂]	1.199,	Cis	<i>i</i>	[Co(en) ₂ Cl(NO)](ClO ₄)	1.356	Trans	<i>pp</i>
	1.195			[Co(en) ₂ Cl ₂](NO ₃)	1.359	Trans	<i>qq</i>
[Mn(NH ₂ NHCOO) ₂ (H ₂ O) ₂]	1.220	Cis	<i>j</i>	[Co(en) ₂ Cl ₂]Cl·H ₂ O	1.360, 1.367	Cis	<i>rr</i>
(NH ₄) ₃ [VO ₂ (C ₂ O ₄) ₂]·2H ₂ O	1.231	Cis	<i>k</i>	[Mn(acac) ₂ (H ₂ O) ₂]	1.363	Trans	<i>ss</i>
[Ti(oxine) ₂ Cl ₂]	1.244	Cis	<i>l</i>		1.368	Trans	<i>tt</i>
[Ti(dieth) ₂ Br ₂][TiBr ₄ (dieth)]	1.238,	Cis	<i>m</i>	[Co(en) ₂ (NCS)(SO ₃)·2H ₂ O	1.363, 1.347	Trans	<i>uu</i>
	1.248			[Ni(diars) ₂ Cl ₂]Cl	1.367	Trans	<i>vv</i>
[Zn(HOCH ₂ COO) ₂ (H ₂ O) ₂]	1.248	Cis	<i>n</i>	[Co(en) ₂ Br ₂]Br·HBr·2H ₂ O	1.370	Trans	<i>ww</i>
[Ga(bipy) ₂ Cl ₂][GaCl ₄]	1.250	Cis	<i>o</i>	[Co(en) ₂ Cl ₂](S ₆ O ₆)H ₂ O	1.377	Trans	<i>xx</i>
[Zn(NH ₂ NHCOO) ₂ (N ₂ H ₄) ₂]	1.256	Trans	<i>p</i>	[Co(en) ₂ (N ₃) ₂](NO ₃)	1.377, 1.402	Cis	<i>yy</i>
[Co(DMG) ₂ (NH ₃) ₂ (NO ₃)	1.26	Trans	<i>q</i>	[Co(pn) ₂ (NO ₂) ₂]Cl	1.377, 1.414	Cis	<i>zz</i>
[Co(NH ₂ COCOO) ₂ (H ₂ O) ₂]·2H ₂ O	1.261	Trans	<i>r</i>	[Ni(diars) ₂ I ₂]	1.383	Trans	<i>aaa</i>
[Ni(MeOCH ₂ COO) ₂ (H ₂ O) ₂]	1.282	Trans	<i>s</i>	[Co(tn) ₂ (NO ₂) ₂](NO ₃)	1.386	Trans	<i>bbb</i>
[Ni(C ₅ H ₄ NCONH ₂) ₂ (H ₂ O) ₂]Cl ₂	1.287	Trans	<i>t</i>	[Ni(tn) ₂ (H ₂ O) ₂](ClO ₄) ₂	1.388	Trans	<i>ccc</i>
[Zn(NH ₂ COCOO) ₂ (H ₂ O) ₂]	1.288	Trans	<i>u</i>	[Co(diars) ₂ Cl ₂](ClO ₄)	1.389	Trans	<i>ddd</i>
[Ni(biimid) ₂ (H ₂ O) ₂](NO ₃) ₂	1.295	Trans	<i>v</i>	[Co(pn) ₂ Cl ₂]Cl·HCl·2H ₂ O	1.399	Trans	<i>eee</i>
[Ni(NH ₂ NHCOO) ₂ (H ₂ O) ₂]	1.296	Trans	<i>w</i>	[Mg(acac) ₂ (H ₂ O) ₂]	1.402	Trans	<i>fff</i>
[Ni(NH ₂ CH(CH ₂ OH)COO) ₂ (H ₂ O) ₂]	1.296	Trans	<i>x</i>	[Co(acac) ₂ (py) ₂]	1.412	Trans	<i>ggg</i>
[Ni(NH ₂ CH ₂ COO) ₂ (H ₂ O) ₂]	1.300	Trans	<i>y</i>	[Ni(acac) ₂ (pyO) ₂]	1.415, 1.417	Cis	<i>hhh</i>
[Co(bipy) ₂ Cl ₂][CoCl ₄]	1.303	Cis	<i>z</i>	[Re(acac) ₂ Cl ₂]	1.425	Trans	<i>iii</i>
[Zn(oxine) ₂ (H ₂ O) ₂]	1.306	Trans	<i>aa</i>	[Ni(NH ₂ CH ₂ CH ₂ COO) ₂ (H ₂ O) ₂]	1.431	Trans	<i>jjj</i>
[Ru(en) ₂ (N ₃)(N ₂)](PF ₆)	1.307	Trans	<i>bb</i>	[Ni(sal) ₂ (H ₂ O) ₂]	1.439	Trans	<i>kkk</i>
[Ni(S ₂ PPh ₂) ₂ (py) ₂]	1.307	Trans	<i>cc</i>	[Co(acac) ₂ (H ₂ O) ₂]	1.439	Trans	<i>lll</i>
[Ni(S ₂ P(OEt) ₂)(py) ₂]	1.308	Trans	<i>dd</i>	[Ni(acac) ₂ (py) ₂]	1.442	Trans	<i>mmm</i>
[Ni(en) ₂ (NCS) ₂]	1.31	Trans	<i>ee</i>	[Ni(acac) ₂ (H ₂ O) ₂]	1.444	Trans	<i>nnn</i>
[Ni(NH ₂ CMe ₂ COO) ₂ (H ₂ O) ₂]·2H ₂ O	1.323,	Cis	<i>ff</i>	[Ni(pn) ₂ (H ₂ O) ₂](NO ₃) ₂	1.450	Trans	<i>ooo</i>
	1.327			[Ni(salim) ₂ (H ₂ O) ₂]	1.460	Trans	<i>ppp</i>
[Zn(NH ₂ CONHNH ₂) ₂ Cl ₂]	1.325	Trans	<i>gg</i>	[Co(tn) ₂ Cl ₂]Cl·HCl·2H ₂ O	1.47	Trans	<i>qqq</i>
[Ni(en) ₂ (NO ₂) ₂]	1.336	Trans	<i>hh</i>	[Zn(C ₅ H ₄ NCOO) ₂ (H ₂ O) ₂]	1.523	Trans	<i>rrr</i>

^a Ligand abbreviations: py, pyridine; *o*-phen, *o*-phenanthroline; oxine, anion of 8-hydroxyquinoline; dieth, 1,2-dimethoxyethane; bipy, 2,2'-bipyridyl; DMG, dimethylglyoxime; biimid, 2,2'-biimidazole; en, ethylenediamine; dimeen, dimethylethylenediamine; acac, acetylacetonate; diars, *o*-phenylenebis(dimethylarsine); pn, 1,2-propylenediamine; tn, trimethylenediamine; pyO, pyridine 1-oxide; sal, salicylaldehyde; salim, salicylaldehyde; *b* R. Stomberg, *Ark. Kemi*, **22**, 29 (1964). ^c I. B. Svensson and R. Stomberg, *Acta Chem. Scand.*, **25**, 898 (1971). ^d R. D. Drew and F. W. B. Einstein, *Inorg. Chem.*, **11**, 1079 (1972). ^e F. A. Cotton and R. H. Soderberg, *J. Amer. Chem. Soc.*, **85**, 2402 (1963). ^f A. L. Beauchamp, B. Saperas, and R. Rivest, *Can. J. Chem.*, **49**, 3579 (1971). ^g C. S. Harrel, and E. O. Schlemper, *Acta Crystallogr., Sect. B*, **27**, 1964 (1971). ^h A. Domenciano, A. Vacicgo, L. Zambonelli, P. L. Loader, and L. M. Venanzi, *Chem. 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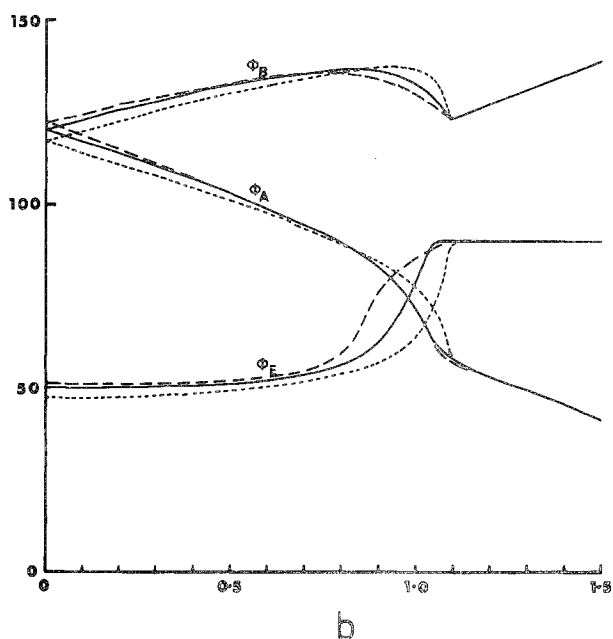


Figure 5. Angular parameters in degrees for skew trapezoidal bipyramidal-trans octahedral $M(\text{bidentate})_2(\text{monodentate})_2$ as a function of normalized ligand bite, b : dotted line, $n = 1$; full line, $n = 6$; broken line, $n = 12$.

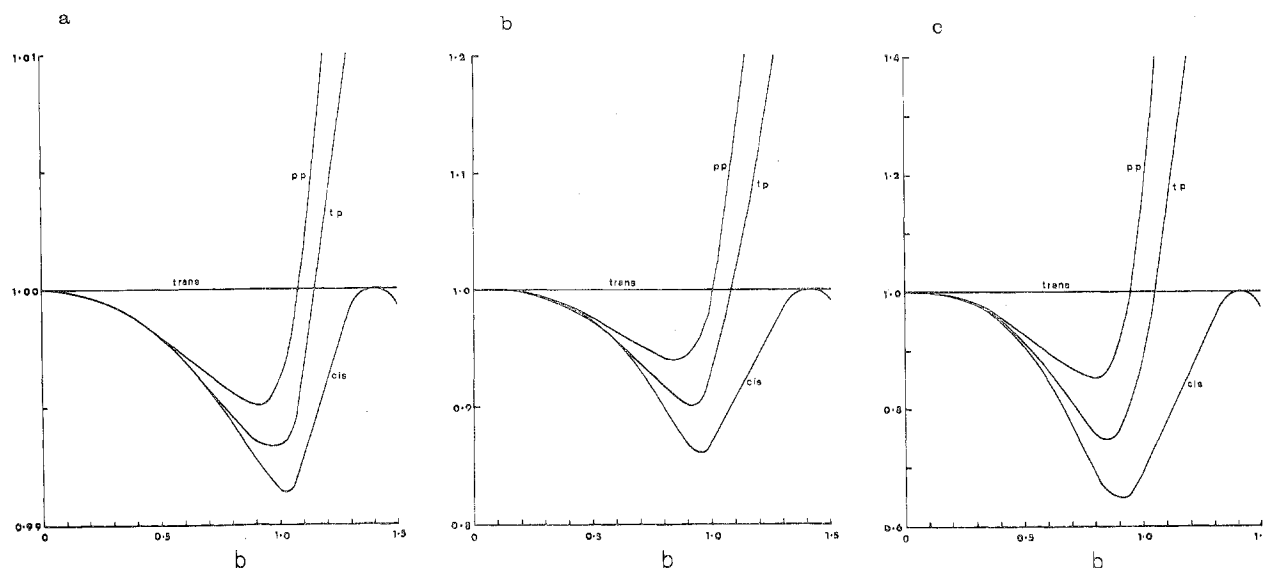


Figure 6. Ligand-ligand repulsion energy coefficients X normalized to those of the skew trapezoidal-bipyramidal-trans octahedral structure, for the cis octahedral (cis), pentagonal-pyramidal (pp), and trigonal-prismatic (tp) structures, as a function of normalized ligand bite, b : (a) $n = 1$; (b) $n = 6$; (c) $n = 12$.

bipyramid is transformed into the trans octahedral structure at $b = 1.11$, 1.06, and 1.08 for $n = 1$, 6, and 12, respectively.

Discussion

It can be seen from Figure 6 that as the normalized bite of the bidentate ligands is increased from 0.0 to 0.8, the cis octahedral structure is the most stable isomer. However the pentagonal pyramid and trigonal prism have only slightly lower stabilities, the ratio of the energy coefficients being in the range 1.00-1.04 for $n = 6$. These three stereochemistries differ only in the rotation of each of these small bidentates about the axis joining the center of each bidentate to the metal atom.

As the normalized bite of the bidentate ligands is further

increased from 0.95 to 1.25, the cis octahedral structure becomes significantly more stable than the other three isomers.

Above normalized bites of 1.25, the cis and trans octahedral structures are of comparable stability and are significantly more stable than the other two isomers.

Those compounds of stoichiometry $M(\text{bidentate})_2(\text{monodentate})_2$ with known crystal structures are listed in order of ascending normalized bite in Table II.

It can be seen that the compounds clearly arrange themselves in three distinct structural groups, which can be rationalized from the above calculations.

The only three compounds with bidentates of normalized bite less than 0.8 have the pentagonal-pyramidal structure.

All eleven compounds containing bidentates of normalized bite in the range 0.95-1.25 have the cis octahedral structure in accordance with the above predictions. This destabilization of the trans octahedral structure compared with the cis octahedral structure is undoubtedly an important reason for the scarcity of trans complexes with many rigid bidentates of small bite and is quite apart from the steric interactions between parts of the bidentates which are more remote from the metal atom than are the donor atoms.⁴

The remaining 48 compounds listed in Table II have a random mixture of cis and trans octahedral structures which is again as expected.

Compounds of copper(II) and of the second- and third-row

transition metal ions with the d^8 electron configuration have been excluded from Table II. This is because the range of metal-ligand distances in these compounds leads to uncertainties in the coordination number and because the basically square-planar four-coordinate structure frequently observed for these ions is not that predicted from simple considerations of ligand-ligand repulsion energies.

Detailed comparisons between the experimentally determined stereochemistries for the compounds in Table II and these calculations are not warranted because of the introduction of uncertainties due to the difference in character between the donor atoms. Nevertheless some general com-

ments may be made about the pentagonal-pyramidal and cis octahedral structures.

Pentagonal Pyramid. The known pentagonal-pyramidal molecules are restricted to bis(peroxo) complexes, in which the peroxo ligands form part of the puckered pentagonal plane. The maximum deviations from the best least-squares plane through ABCDE are $\pm 12^\circ$, $\pm 3^\circ$, and $\pm 7^\circ$, respectively, for the three compounds listed in Table II, which are less than the predicted value of $\pm 16^\circ$. This may be partly due to the very short metal-apical oxygen bonds and/or to the quasi-pentagonal-bipyramidal nature of these molecules. In $(\text{NH}_4)_4[(\text{V}(\text{O}_2)_2\text{O})_2\text{O}]$ there are six vanadium-oxygen bonds in the range 1.61–2.01 Å, but one of the peroxo oxygen atoms bonded to the other vanadium atom in the dimeric anion approaches to 2.50 Å to complete the pentagonal bipyramid. Similarly in $(\text{NH}_4)[\text{V}(\text{O}_2)_2\text{O}(\text{NH}_3)]$ there are five vanadium-oxygen bonds in the range 1.61–1.88 Å, but the vanadyl oxygen atom of an adjacent molecule occupies the seventh position creating a vanadium-oxygen distance of 2.93 Å.

Cis Octahedral Structures. These calculations lead to the interesting prediction that the cis octahedral structure will be distorted in a way which is significantly different from that which might have been intuitively expected.

Commencing with a regular octahedral $\text{cis-M}(\text{bidentate})_2$ - $(\text{monodentate})_2$ with a normalized bidentate bite of 1.414, at first sight it might be expected that a decrease in bite would simply result in the atoms A and B (and also the symmetry-related C and D) moving toward one another along the AB edge (and CD edge, respectively). That is, there would be expected to be an increase in ϕ_A and a decrease in θ_A , with a simultaneous decrease in ϕ_B and increase in θ_B . The effect on the bond angles about the metal atom M would be to increase AMC and AME, whereas AMF, BMC, and BMF would be relatively unchanged. The coordinate ϕ_E and the bond angle EMF (which is equal to twice ϕ_E) would also be expected to increase as the other four donor atoms become more crowded together.

However an important prediction from these calculations is that this contraction in the bite from 1.414 to 0.7 is accompanied by a rotation of the bidentates about the twofold axis of the molecule resulting in a much larger distortion of the polyhedron. That is, in addition to the expected increase in ϕ_A , there is an initial increase in θ_A (Figure 2). The increase in θ_B is consequently fairly large, whereas ϕ_B is approximately constant. (These results have been anticipated in Figure 1). In terms of bond angles, the increase in θ_A and θ_B results in an increase in AMF as well as in AMC and AME, whereas BMF remains close to 90° . No prediction can be made about BMC, since the ligand-ligand repulsion energy is relatively insensitive to this angle and also because the angle corresponding to minimum energy depends upon the assumed value of n in the repulsive law.

This predicted increase in θ_A and θ_B on shrinking the bidentate is confirmed by experiment. The stereochemistry of the cis octahedral complex containing bidentates of smallest normalized bite, namely, $[\text{Co}(\text{NO}_3)_2(\text{Me}_3\text{PO})_2]$, cannot be adequately described as "distorted octahedral." In this case $\theta_A = 17^\circ$, and the relevant bond angles are AMC = 105° , AME = 96° , AMF = 96° , BMF = 91° , and BMC = 85° .

Acknowledgments. This work was carried out while on leave at the University Chemical Laboratories, University of Cambridge, and thanks are due to Professor J. Lewis and his colleagues for their hospitality.

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Dimeric Triphenylphosphine Complexes of Platinum(II)

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Received November 15, 1972

During the course of attempting to prepare $\text{trans}[(\text{PPh}_3)_2\text{Pt}_2\text{Cl}_4]$, which is orange, by a modification of the method described in ref 1, we prepared a new pale-yellow isomer which we consider to be $\text{cis}[(\text{PPh}_3)_2\text{Pt}_2\text{Cl}_4]$. Since one of the main uses² of these bridged complexes involves their reaction with a further ligand to yield monomeric complexes $[(\text{PPh}_3)\text{Pt}(\text{LCl}_2)]$, we investigated the reaction of the new isomer with *p*-toluidine and carbon monoxide.

Experimental Section

Preparation of $[(\text{PPh}_3)_2\text{Pt}_2\text{Cl}_4]$. Method 1. $\text{cis}[(\text{PPh}_3)_2\text{PtCl}_2]$ ³ (10 mmol) and PtCl_2 (11 mmol) were refluxed in tetrachloroethane (150 ml) for 6 hr. After filtering to remove unreacted PtCl_2 the solution was cooled to 0° and treated with animal charcoal to remove the small amount of colloidal platinum formed. Light petroleum (ca. 200 ml, bp $60\text{--}80^\circ$) was then added with vigorous stirring to give a pale-yellow precipitate in 75% yield. Anal. Calcd for $[(\text{PPh}_3)_2\text{Pt}_2\text{Cl}_4]$: C, 41.0; H, 2.9. Found: C, 41.0; H, 3.0. The principal parent ion peak in the mass spectrum was at 1056 (calcd mol wt = 1056.6).

Method 2. Following the procedure in ref 1, $\text{cis}[(\text{PPh}_3)_2\text{PtCl}_2]$ ³ (0.92 mmol) and PtCl_2 (1.10 mmol) were refluxed with stirring under nitrogen in tetrachloroethane (25 ml) for 1 hr. After filtering to remove unreacted PtCl_2 , treating the solution with animal charcoal, and evaporating to 5 ml under reduced pressure, a pale yellow crystalline solid contaminated with some colloidal platinum was obtained. Further pale yellow crystals were obtained by the addition of pentane. Following the procedure in ref 1, the product was purified by dissolving in chloroform, treating the solution with animal charcoal, and adding pentane to precipitate orange $[(\text{PPh}_3)_2\text{Pt}_2\text{Cl}_4]$ in 50% yield. Anal. Calcd for $[(\text{PPh}_3)_2\text{Pt}_2\text{Cl}_4]$: C, 41.0; H, 2.9. Found: C, 40.8; H, 2.8.

Isomerization of $[(\text{PPh}_3)_2\text{Pt}_2\text{Cl}_4]$. Yellow Isomer. When a solution of yellow $[(\text{PPh}_3)_2\text{Pt}_2\text{Cl}_4]$ was warmed in chloroform it rapidly turned orange with precipitation of the orange isomer. After boiling for 5 min quantitative conversion of the yellow isomer to the orange was achieved. The orange isomer was shown to be $\text{trans}[(\text{PPh}_3)_2\text{Pt}_2\text{Cl}_4]$ by comparison with an authentic sample prepared as described by Goodfellow and Venanzi.⁴

Orange Isomer. When a solution of orange $[(\text{PPh}_3)_2\text{Pt}_2\text{Cl}_4]$ was refluxed in tetrachloroethane, it darkened due to the formation of a little colloidal platinum. After refluxing for 1 hr the solution was cooled to room temperature and treated with animal charcoal and the resulting yellow filtrate cooled in an ice bath to yield pale yellow crystals of $[(\text{PPh}_3)_2\text{Pt}_2\text{Cl}_4]$. Further pale yellow crystals were obtained by the addition of light petroleum to the mother liquor. The infrared spectra were identical with that of the yellow isomer of $[(\text{PPh}_3)_2\text{Pt}_2\text{Cl}_4]$.

Reaction of $[(\text{PPh}_3)_2\text{Pt}_2\text{Cl}_4]$ with *p*-Toluidine. 1. **Yellow Isomer.** When a solution of the yellow isomer of $[(\text{PPh}_3)_2\text{Pt}_2\text{Cl}_4]$ (0.187 mmol) in acetone was treated with a solution of *p*-toluidine (0.373 mmol) in acetone, a yellow precipitate of $\text{cis}[(\text{PPh}_3)\text{Pt}(\text{p-toluidine})\text{Cl}_2]$ was obtained in 98% yield. The precipitate was filtered off, dried, and recrystallized from an acetone-petroleum ether (bp $60\text{--}80^\circ$) mixture. Anal. Calcd for $[(\text{PPh}_3)\text{Pt}(\text{p-toluidine})\text{Cl}_2]$: C, 47.3; H, 3.8; N, 2.2. Found: C, 47.1; H, 3.7; N, 2.0. The melting point was $247\text{--}249^\circ$ (without decomposition). The observation of two Pt-Cl stretching vibrations in the far-infrared (Nujol mull) at 348.5 and 327 cm^{-1} , together with a dipole moment (in benzene at 25.2°) of 2.47 D, indicated that the product was the cis isomer.

2. **Orange Isomer.** A suspension of the orange isomer of

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