Table XII. Unit-Weighted Least-Squares Planes for (η^3-2-methylallyl)PdCl(PPh_3)

plane	atoms	dist from plane, Å
1	C(1), C(2), C(3)	0.00
	C(4)	-0.230 (7)
	Pd	-1.717 (1)
	H(1s)	-0.15 (5)
	H(1a)	0.27 (5)
	H(3a)	0.58 (7)
	H(3s)	-0.25 (5)
2	C(1), H(1s), H(1a)	0.00
3	C(3), H(3s), H(3a)	0.00
4	C(2), C(1), H(1s)	0.00
5	C(2), C(1), H(1a)	0.00
6	C(2), C(3), H(3a)	0.00
7	C(2), C(3), H(3s)	0.00

planes	dihedral angle, deg	planes	dihedral angle, deg
1-2	20	1-5	22
1-3	36	1-6	42
1-4	11	1-7	19

The hydrogen atoms were included and refined to converge to the residuals and parameters given in Table VIII. The values of the fractional coordinates are listed in Table IX. Selected bond lengths and angles and the esd's obtained from the inverse matrix obtained on the final cycle of refinement are given in Tables X and XI. Least-squares planes are given in Table XII. Tables of anisotropic thermal parameters, structure factor amplitudes, and phenyl parameters are available in the supplementary material.

The disordered solvent and anion in the crystal of **2** prevented a satisfactory solution of the structure for use in accurate bond length determinations. We hope that a satisfactory crystal may be obtained with other counterions in the future. The coordinates for this structure are also included in the supplementary material.

Acknowledgment. We wish to thank the NSF for support of this research.

Registry No. **1**, 99232-27-6; **2**, 99212-69-8; **3**, 99212-71-2; **4**, 99212-73-4; **5**, 99232-29-8; **6a**, 99212-75-6; **6b**, 99266-43-0; **7**, 99232-31-2; **8**, 99232-33-4; **9**, 12098-21-4; $PCoBF^+BF_4^-$, 34323-77-8; $PZnBF^+BF_4^-$, 28042-05-9; CH_2CHCD_2OH, 10475-51-1; CH_2CHCD_2Cl, 37730-14-6; [(η^3-allyl)PdCl(PPh_3)], 12097-84-6; [(η^3-allyl)PdCl(PZnBF)][BF_4], 99212-77-8; [(η^3-allyl)PdCl]$_2$, 12012-95-2; [(η^3-2-methylallyl)PdCl]$_2$, 12081-18-4; [(η^3-1-methylallyl)PdCl]$_2$, 12081-22-0; [(η^3-1,1-dimethylallyl)PdCl]$_2$, 12288-41-4; [(η^3-1,3-dimethylallyl)PdCl]$_2$, 12245-05-5; [(η^3-1-acetyl-2-methylallyl)PdCl]$_2$ (isomer 1), 31832-96-9; [(η^3-1-acetyl-2-methylallyl)PdCl]$_2$ (isomer 2), 31869-20-2; [(η^3-cyclohexenyl)PdCl]$_2$, 12090-09-4; [(η^3-cycloheptenyl)PdCl]$_2$, 35284-32-3.

Supplementary Material Available: Tables of calculated and observed structure factor amplitudes, anisotropic thermal parameters (B_{ij}'s), selected phenyl bond angles for (2-methylallyl)PdCl(PPh_3), and positional and thermal parameters for (2-methylallyl)PdCl(*PCoBF*) (14 pages). Ordering information is given on any current masthead page.

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Ligand-Field Parameters and the Stereochemical Activity of d Shells in Trigonal-Bipyramidal Complexes of the First Transition Series†

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Angular-overlap-model analyses of the trigonal-bipyramidal (TBP) complexes [M(Me_6tren)Br]Br (M = Cr, Fe, Co, Ni, Cu; Me_6tren = tris((dimethylamino)ethyl)amine) and for [Cu(tren)NH_3](ClO_4)$_2$ (tren = tris(aminoethyl)amine) are reported. Changes in the ligand-field parameters and detailed bond length variations throughout the complete Me_6tren series chromium to zinc describe a situation dominated by the variable d^n configuration. The possibility that the relatively low ligand-field strengths of the equatorial ligands in TBP complexes of copper(II) may arise from (negative) contributions by in-plane coordination voids rather than from the stereochemical activity of the d^9 shell is shown to be untenable.

Introduction

Ligand-field analyses[1] of [Cu(bpy)$_2$I]I and [Cu(phen)$_2H_2O$](NO_3)$_2$ (bpy = 2,2'-bipyridyl; phen = 1,10-phenanthroline), have established markedly greater axial than equatorial angular-overlap-model (AOM) parameter values for these unsaturated chelates despite closely similar copper-nitrogen bond lengths. There is obviously no simple relationship between bond length and the magnitude of ligand-field parameters in these systems: in fact, the asymmetric chelation from these ligands arises from the stereochemical activity of the incomplete d shell.

More detailed comparisons between the AOM parameters for these two complexes center on the role of coordination voids, which have been shown[2] to be important in tetragonal copper(II) systems. We have argued that the low e_σ value for the equatorial water ligand in the phen complex reflects a significant, negative ligand-field contribution from the partially void region opposite. In this molecule the N_{eq}-Cu-N_{eq} angle is 140° whereas for the bpy complex it is 114°. The negative ligand field of a coordination void arises, not from empty space, but from that portion of metal s electron density that is essentially not preempted by bonding to adjacent ligands.[3,4] The ligand-field role of a void cell will thus be determined in large measure by the angle subtended by the neighboring ligands, and we expect that the quantitative contribution will vary with this geometrical feature in a strongly nonlinear way. In the phen complex, the 140° angle defines a region that is apparently large enough to exert a noticeable effect. Although we do not envisage a significant void contribution in the bpy complex, one *could* argue that the large difference between the AOM parameter values for the axial and equatorial sites in these TBP systems is due solely to the 120° angles subtended opposite the equatorial ligands. We have therefore sought systems for which ligand-field analyses can resolve this issue with clarity. The present study describes analyses for the complexes [M(Me_6tren)Br]Br (M^{II} = Cr, Mn, Co, Ni, Cu, Zn; Me_6tren = tris((dimethylamino)ethyl)amine), which comprise a series of isomorphous TBP molecules. The closely related compound [Cu(tren)NH_3](ClO_4)$_2$, tren = tris(aminoethyl)amine, offers further opportunity for comparison (Figure 1).

Fitting

The ligand-field analyses described here are based upon the angular-overlap model as reformulated by Gerloch and Woolley.[3-6] All

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† No reprints available from this laboratory.

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Table I. Geometrical (Å and deg) and Best-Fit Ligand-Field (cm^{-1}) Parameters for [M(Me$_6$tren)Br]Br Complexes (ζ = 0 cm^{-1})

	M													
	Cr		Mn		Fe		Co		Ni		Cu		Zn	
M-N$_{ax}$	-		2.19		2.21		2.151		2.10		2.07		2.19	
M-N$_{eq}$	-		2.27		2.15		2.080		2.13		2.14		2.11	
M-Br	-		2.491		2.482		2.431		2.467		2.393		2.449	
N$_{eq}$-M-N$_{eq}$	-		117.4		117.8		117.6		119.0		119.1		118.4	
e_σ(AX)	6000	6200	-	-	3750	4000	3700	4000	4700	5000	5600	4800	-	-
e_σ(N$_{eq}$)	2800	3600	-	-	3500	4000	3400	4000	3400	3900	2400	3300	-	-
e_π(Br)	0	1000	-	-	0	1000	0	1000	0	1000	0	1000	-	-
B	-	-	-	-	-	-	740	720	800	800	-	-	-	-
Σ	20400	25200	-	-	18000	22000	17600	22000	19600	23700	18400	23500	-	-
confign	d^4		d^5		d^6		d^7		d^8		d^9		d^{10}	

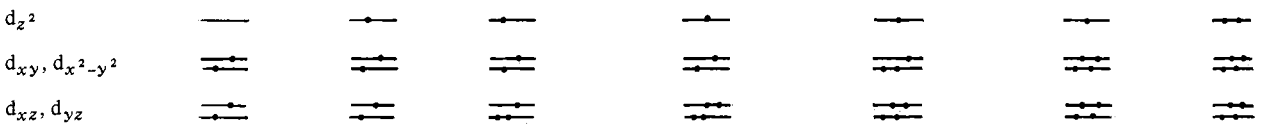

Table II. Comparison between Typical Calculated and Observed Transition Energies (cm^{-1}): e_π(Br) Taken as 1000 cm^{-1} for Illustration (ζ = 0 cm^{-1})

Cr		Fe		Co		Ni		Cu	
calcd	obsd	calcd	obsd	calcd	obsd	calcd	obsd	calcd	obsd
14 005	14 000	3898	3800	3 662	-	6 904	7 100	10 124	10 000
14 004		3899		5 120	-	6 905		10 125	
10 787	10 800	9717	9800	5 393	5 600	10 364	10 500	12 992	12 800
10 795				5 393		11 653	11 400^a	12 993	
				12 652	12 300	14 116	14 100		
				12 653		20 051	20 000		
				16 667	16 200	20 052			
				19 214	18 900-19 600	22 479	22 700		
				19 214					

^{a} Band observed in solution spectrum.

calculations were performed by using the standard techniques and computer package[7] previously described, with basis sets comprising all free-ion terms of maximum spin multiplicity: parametrization of interelectron repulsion and spin–orbit coupling involves the Racah B and the spin–orbit coupling coefficient, ζ, respectively. Unless otherwise stated, however, ζ is taken to be zero. For each system, the molecular geometries determined from single-crystal X-ray studies were employed, except in the case of chromium, for which that of the copper complex was used.

[M(Me$_6$tren)Br]Br (M = Cr, Fe, Co, Ni, Cu)

The complexes [M(Me$_6$tren)Br]Br, where M = Cr, Fe, Co, Ni, and Cu, comprise five members of an extended series of high-spin, isomorphous compounds. Ligand-field analyses seek to reproduce reported diffuse-reflectance band maxima[8-10] supplemented, in the case of the nickel analogue, by (unpolarized) single-crystal transmission[11] and solution spectral data.[8]

Throughout the series, the nearly regular TBP coordination geometry is closely similar: in particular, each molecule has crystallographic C_3 symmetry with the bromine and central nitrogen of the Me$_6$tren ligand collinear with the metal ion.[12-14] Meaningful AOM parameter values for these axial ligands can, therefore, only be averages. In view of the non-π-bonding function of the axial nitrogen, however, we have chosen to use the parameter set e_σ(AX) and e_π(Br) together with e_σ(N$_{eq}$) for the equatorial donors. Since there are only two orbital splittings not determined by the rigorous C_3 symmetry of these complexes, our ligand-field modeling is underdetermined, regardless of the d^n configuration. This will be manifested in correlations between the fitting values of the three AOM parameters chosen. In many other AOM analyses, correlations between parameter values may be bounded by implicit conditions imposed by the low molecular symmetry. For the exact high symmetry here, no such bounds exist. The relationships between the best-fit parameter values have been determined, and they are illustrated by the representative data in Table I. In Table II, the calculated and observed transition energies for the parameter sets with e_π(Br) = 1000 cm^{-1} are compared. Equally acceptable agreement is obtained for e_σ(AX) and e_σ(N$_{eq}$) in the range ±300 cm^{-1} and B in the range ±60 cm^{-1} of the quoted values. Inclusion of spin–orbit coupling has little effect on the best-fit AOM parameter values. For example, as ζ changes from 0 to 650 cm^{-1}, the best-fit values for the nickel complex change by less than 200 cm^{-1}.

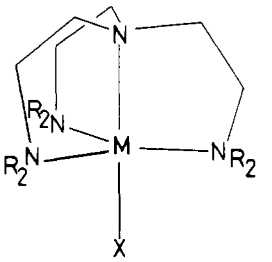

Figure 1. Coordination geometry in tren and Me$_6$tren complexes:
M = Cr, Mn, Fe, Co, Ni, Cu, Zn; R = Me; X = Br
M = Cu; R = H; X = NH$_3$

We have not attempted an analysis of the manganese system partly due to the increased number of parameters required (both Racah parameters B and C must be varied) but especially in view

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Table III. Geometrical (Å and deg) and Best-Fit Ligand-Field (cm^{-1}) Parameters and Calculated and Observed Transition Energies (cm^{-1}) for $[Cu(tren)NH_3](ClO_4)_2$ ($\zeta = 0$ cm^{-1})

				transition energies	
param	value	param	value	calcd	obsd
$Cu-N_{ax}$	2.041	$e_\sigma(AX)$	6400	15 160	15 200
$Cu-NH_3$	2.023	$e_\sigma(N_{eq})$	3300	15 160	
$Cu-N_{eq}$	2.082	Σ	22700	11 396	11 400
$N_{eq}-Cu-N_{eq}$	119			11 396	

of the present computational costs of performing calculations for the d^5 configuration.

As part of a study[15] of the paramagnetism of $[Ni(Me_6tren)Br]Br$, Banci et al. report AOM parameter values deduced from an analysis of the optical spectrum. Separate values are quoted for $e_\sigma(Br)$ and $e_\sigma(N_{ax})$, a distinction between these holohedrally related[16] ligands that can be made only by recourse to untenable relationships between AOM e_λ parameters and the squares of overlap integrals. A similar approach has been followed[17] for the cobalt(II) analogue also. Nevertheless, the published values, which lie somewhat from the correlation described above, are not seriously different on these occasions.

$[Cu(tren)NH_3](ClO_4)_2$

The C_3 coordination geometry[18] of $[Cu(tren)NH_3](ClO_4)_2$ is very similar to those of the Me_6tren complexes described above. Our ligand-field analysis is analogous except that we assume no π interaction with the axial ammonia ligand, leaving $e_\sigma(AX)$ and $e_\sigma(N_{eq})$ as the only AOM parameters. Again, we seek to reproduce reported[18] diffuse-reflectance band maxima. Table III gives best-fit AOM parameter values together with a comparison between observed and calculated transition energies. Equally good reproduction of the spectrum is obtained for values of $e_\sigma(AX)$ and $e_\sigma(N_{eq})$ within 150 and 500 cm^{-1}, respectively, of the given values. The best-fit AOM parameter values are not very sensitive to spin-orbit coupling, $e_\sigma(AX)$ and $e_\sigma(N_{eq})$ decreasing by essentially nothing and ca. 300 cm^{-1}, respectively, as ζ increases from 0 to 700 cm^{-1}.

Discussion

In the systems $[Cu(bpy)_2I]I$, $[Cu(phen)_2H_2O](NO_3)_2$, and $[Cu(tet\text{-}b)(o\text{-}mercaptobenzoate)]\cdot H_2O$, the AOM parameters describe a markedly greater axial than equatorial perturbation.[1] Two possible factors may be considered to be responsible for this large difference: (i) the stereochemical activity of the incomplete d shell; (ii) associated with the larger equatorial bond angles, a (negative) void cell contribution to the equatorial ligand-field parameters. While some combination of these two mechanisms might be anticipated a priori, the bond lengths and AOM parameter values given in Table I indicate a virtual irrelevance of the second. Thus, for the copper complex of Me_6tren, the single hole in the d_{z^2} orbital is accompanied by an axially compressed geometry contrary to the predictions of the closed-shell theory of Gillespie and Nyholm,[19] in which an axially elongated geometry like that of the zinc analogue[14] would be anticipated. Moreover, the value of $e_\sigma(AX)$ for the copper complex is again much greater than the value of $e_\sigma(N_{eq})$. For a ligand field in this complex dominated by the influence of coordination voids in the equatorial plane, such a difference in AOM parameter values may well be reasonable but the observed compressed geometry would be unexpected. It should also follow that the void cell contribution be more or less independent of d^n configuration—this has been established[20] for square-planar complexes—so that a similarly large difference in ligand-field parameter values should obtain across the series. The data in Table I for the cobalt analogue, for example, clearly show that such is not the case. However, the observed bond lengths and AOM parameter values can be rationalized quite simply on the basis of the stereochemical activity of d electrons. Consider, then, the d-orbital splitting pattern appropriate for these systems.

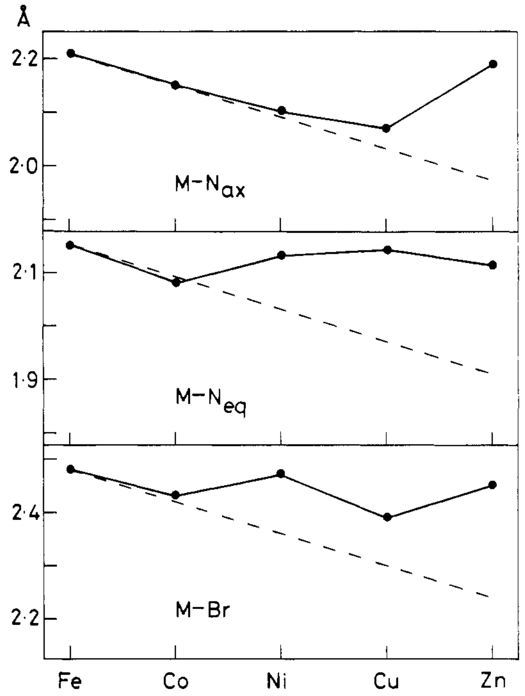

Figure 2. Variation in metal-ligand bond lengths for the Me_6tren complexes (solid lines). The broken lines represent estimated bond length decrease arising from variations in Z_{eff} alone (see text).

In the threefold symmetry of these complexes, the d orbitals split into three sets which are, in order of decreasing energy, $d_{z^2} > d_{xy}, d_{x^2-y^2} > d_{xz}, d_{yz}$. This pattern, together with the purely σ-bonding role of the Me_6tren ligand and the approximate coplanarity of the equatorial ligands with the central metal, provides a ready separation of σ- and π-bonding effects. Thus the d_{z^2} orbital is principally involved with axial σ interactions and the d_{xy} and $d_{x^2-y^2}$ orbitals are essentially involved with equatorial σ interactions whereas the d_{xz} and d_{yz} orbitals are involved with the π interaction from the bromide ligand. In both iron and cobalt systems there is a symmetrical distribution of holes in the σ type orbitals, the extra electron merely being added to the π set. We presume π-bonding influences upon stereochemistry to be relatively unimportant, and this appears to be borne out by the geometrical details in Table I. Both these complexes have similarly axially elongated geometries, as for the closed-shell zinc molecule, together with virtually identical sets of ligand-field parameter values. For nickel, however, there is now an asymmetry in the σ configuration with only one hole in the equatorial plane. The d-electron distribution is intermediate between those of cobalt and copper with bond lengths and AOM parameters also describing an intermediate situation. Note also that this qualitative discussion applies for any reasonable value of $e_\pi(Br)$. On the other hand, the change in relative equatorial and axial bond lengths is not accompanied by a comparable reversal of $e_\pi(AX)$ and $e_\sigma(N_{eq})$. This no doubt reflects the averaged nature of the axial parameters and our expectation that the central nitrogen of Me_6tren is a better donor.

These qualitative observations may now be supplemented with more quantitative appraisals of both bond length variations and ligand-field parameters throughout the series. We being with the geometrical features.

The poor self-shielding of d electrons implies that the monotonic increase in the nulcear charge in crossing the first transition series

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from left to right should be accompanied by a similarly monotonic increase in the effective nuclear charge, Z_{eff}. We would therefore anticipate a general decrease in metal–ligand bond lengths. Superimposed upon this will be the asymmetric influences of the d electrons.

The transition from iron to cobalt involves no change in the σ type configuration so that the general bond length decrease of about 0.6 Å should be mainly associated with an increase in Z_{eff}. For the sake of simplicity and as a rough guide for the present discussion, we have extrapolated this difference in a linear fashion, as shown in Figure 2. From cobalt to copper, electrons are added progressively to the d orbitals lying in the equatorial plane, giving a general increase in the M–N_{eq} bond length. On the other hand, the population of the d_{z^2} orbital remains constant and we observe a general decrease in the M–N_{ax} distance no doubt tempered by the need to balance effects occurring elsewhere in the molecule in line with the demands of the electroneutrality principle. At zinc, the doubly filled d_{z^2} orbital results in a sharp increase in the M–N_{ax} bond length. The metal–bromine distances follow a trend similar to that of M–N_{ax} except at nickel where steric interactions with the equatorial groups result in a bond somewhat longer than otherwise anticipated.

These arguments have also been given by Orioli,[21] who goes on to rationalize the apparently anomalous geometry of the manganese complex in terms of the large size of the metal ion and the geometrical constraints of the ligand, which apparently prevent the attainment of the expected axially elongated geometry for the symmetric d^5 configuration. His argument should apply to chromium as well although, for a d^4 system, we would in any case expect a compressed geometry on electronic grounds by analogy with the d^9 configuration. Certainly, the AOM parameters take much larger axial than equatorial values, as found for copper, but this difference may well arise through a combination of electronic and steric interactions.

The detailed trends in AOM parameters throughout the series revolve around the ligand-field trace, Σ. For a given value of e_π(Br), this sum remains remarkably constant—which we presume reflects the nearly equal electronegativities of the metal ions in this group of complexes. As argued elsewhere[22] we expect Σ to be correlated with the gross transfer of negative charge to the central metal from the ligating set. While some significant variation in Σ might be considered possible on first sight of the data in Table I, the spread is far less if one recognizes the likely similarity of M–Br π interactions throughout the series. A vanishing π perturbation in any of the molecules is unexpected, and comparison with AOM e_π(Br) for other systems[23,24] suggests that values nearer 1000 cm^{-1} are more probable. Furthermore, the (essentially unique) value of 22 700 cm^{-1} established for Σ in $[Cu(tren)NH_3](ClO_4)_2$ compares well with that in the Me_6tren compound for larger values of e_π(Br) although exact equality in the Σ values is not expected, of course (cf. $Cu(tach)_2(ClO_4)_2$ and $Cu(en)_2(BF_4)_2$, which have Σ values of 21 800 and 20 500 cm^{-1}, respectively[2]). If Σ values do indeed increase with the electronegativity of the central metal as expected, a value close to 23 000 cm^{-1} for the copper complexes effectively establishes an upper limit within the series, and hence, by reference to Table I, values of e_π(Br) within a few hundred wavenumbers of 1000.

Finally, we may compare the ligand-field parameters for the two copper molecules reported in this study. First, the value of e_σ(AX) for the tren complex is somewhat larger than that for the Me_6tren analogue. Undoubtedly, this is due to the increased σ-donor role of NH_3 over that of Br and/or the slight decrease in the Cu–N_{ax} bond length. On the other hand and second, the values for $e_\sigma(N_{eq})$ seem to be quite similar despite the appreciably longer bond length in the Me_6tren system. Of course, the equatorial ligands are different and we expect the methylated nitrogen of Me_6tren to be a better donor than the primary amine of tren. We are led, therefore, to suggest that the *inter*active nature of bonding here reveals a change in the acceptor property of the metal-containing moiety every bit as much as one in the donor property of the ligator: in effect, the electroneutrality of the copper atom in the Me_6tren molecule is adequately satisfied by an intrinsically stronger donor but at a larger distance.

Acknowledgment. R.J.D. thanks the Commonwealth Scholarship Commission for financial support.

Registry No. $[Cr(Me_6tren)Br]Br$, 15694-12-9; $[Fe(Me_6tren)Br]Br$, 74220-28-3; $[Co(Me_6tren)Br]Br$, 52225-43-1; $[Ni(Me_6tren)Br]Br$, 57036-60-9; $[Cu(Me_6tren)Br]Br$, 59172-15-5; $[Mn(Me_6tren)Br]Br$, 55684-66-7; $[Zn(Me_6tren)Br]Br$, 74220-29-4; $[Cu(tren)NH_3](ClO_4)_2$, 75094-49-4.

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