Articles

Prediction and Interpretation of Electronic Spectra of Transition Metal Complexes via the Combination of Molecular Mechanics and Angular Overlap Model Calculations

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Received October 15, 1992

The combination of molecular mechanics (MM) and angular overlap model (AOM) calculations has been applied in the prediction of the d–d electronic spectra of a variety of hexaamine complexes of Co(III), Cr(III), and Ni(II). Assuming that the e_σ parameters (equatable with Dq) are directly proportional to r^{-6}, where r is the M–N bond length, a proportionality constant, C, was determined for each type of M–N bond, i.e. $M–NH_3$, $M–NH_2R$, $M–NHR_2$, and $M–NR_3$. The C parameters were found to increase with the addition of each alkyl group for all three systems.

Introduction

The angular overlap model (AOM) and the related cellular ligand field model are popular methods for the interpretation of electronic properties of transition metal coordination compounds.[2] On the basis of the geometry of the chromophore, the experimental data may be fitted with a parametrization which accounts for interelectronic repulsion (F_2 and F_4), spin–orbit coupling (ζ), and various forms of metal–ligand (M–L) bonding. Each individual M–L interaction is modeled with a set of parameters, e_σ and e_π, which account for σ- and π-bonding, respectively. The energy levels are then computed via the angular overlap matrix, viz. an interaction matrix which is adapted to the exact geometry of the chromophore. The magnitudes and signs of the e_σ and e_π parameters obtained from fitting the spectrum are generally interpretable in terms of the nature of the bond; e.g., a large negative value of e_π is indicative of the ligand being a strong π-acceptor. Judicious fitting and interpretation of these parameters have led to well-defined, and chemically reasonable, descriptions of M–L bonding, particularly in mixed-ligand and low-symmetry complexes, where several transitions may be observed.[3–5]

As a consequence of the reliance of the AOM on a prior knowledge of the geometry of the chromophore and the abundance of variables within its parametrization scheme, it has been of little use in predicting the electronic properties of transition metal complexes. The emergence of molecular mechanics (MM) in the field of coordination chemistry has offered a solution to the first problem.[6,7] In the MM model, the geometry of a molecule is refined via a purely mechanical formalism where electronic effects are included but not explicitly; viz., they are not separated from a range of other interactions such as repulsion, electrostatic interactions, etc. Recent force field calculations have shown that the crystallographically determined geometries of a wide range of coordination compounds may be well reproduced within a simple parametrization scheme.[8] The calculated structures do not take into account any interactions outside the coordination sphere such as crystal lattice effects for solid-state structures or solvation and ion pairing for solution chemistry, so it is important that connections are established between the MM-calculated structures and those of the actual complex ions in solution. Successful predictions of equilibrium mixtures of several isomeric systems, specifically Co(III) and Ni(II) complexes, have been made,[9–11] which show that the calculated structures indeed have relevance to solution chemistry.

The second shortcoming of the AOM, as alluded to above, is the large number of variables that must be reduced if one is to employ the method in a predictive role. The issue of transferability of AOM parameters, especially e_σ and e_π, has been a sticking point which has stifled application of the model to the prediction of electronic properties of coordination compounds. Nevertheless, several correlations between e_σ and the M–L distance, r, have been reported,[12–14] where the relationship is usually of the form

$$e_\sigma(r) = C/r^n$$

where $1 \leq n \leq 6$ and C is a constant. Since correlations between e_σ and r evidently exist, it should be possible to fit values of the above constant, C, to a series of related complexes and, if the geometry of the chromophore can be calculated, apply the same constant in the prediction of the spectra of other closely related coordination compounds.

The design of transition metal complexes with specific electronic properties is a long-term objective of this method. As a first step toward this goal, the present study focuses on the prediction of d–d electronic spectra of Co(III), Cr(III), and Ni(II) hexaamine complexes using a combination of MM and AOM calculations.

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(2) Gerloch, M. *Magnetism and Ligand Field Analysis*; Cambridge University Press: Cambridge, U.K., 1984.
(3) Deeth, R. J.; Gerloch, M. *Inorg. Chem.* **1984**, *23*, 3846, 3853.
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(7) Comba, P. *Coord. Chem. Rev.* **1993**, *123*, 1.
(8) Bernhardt, P. V.; Comba, P. *Inorg. Chem.* **1992**, *31*, 2638.
(9) Comba, P.; Hambley, T. W.; Zipper, L. *Helv. Chim. Acta* **1988**, *71*, 1875.
(10) Bernhardt, P. V.; Comba, P.; Gyr, T.; Várnagy, K. *Inorg. Chem.* **1992**, *31*, 1220.
(11) Bernhardt, P. V.; Comba, P.; Hambley, T. W.; Sóvágó, I.; Várnagy, K. *J. Chem. Soc., Dalton Trans.*, in press.
(12) Bertini, I.; Gatteschi, D.; Scozzofava, A. *Inorg. Chem.* **1976**, *15*, 203.
(13) Bencini, A.; Benelli, C.; Gatteschi, D. *Inorg. Chem.* **1983**, *22*, 470.
(14) Lever, A. B. P.; Walker, I. M.; McCarthy, P. J.; Mertes, K. B.; Jircitano, A.; Sheldon, R. *Inorg. Chem.* **1983**, *22*, 2252.

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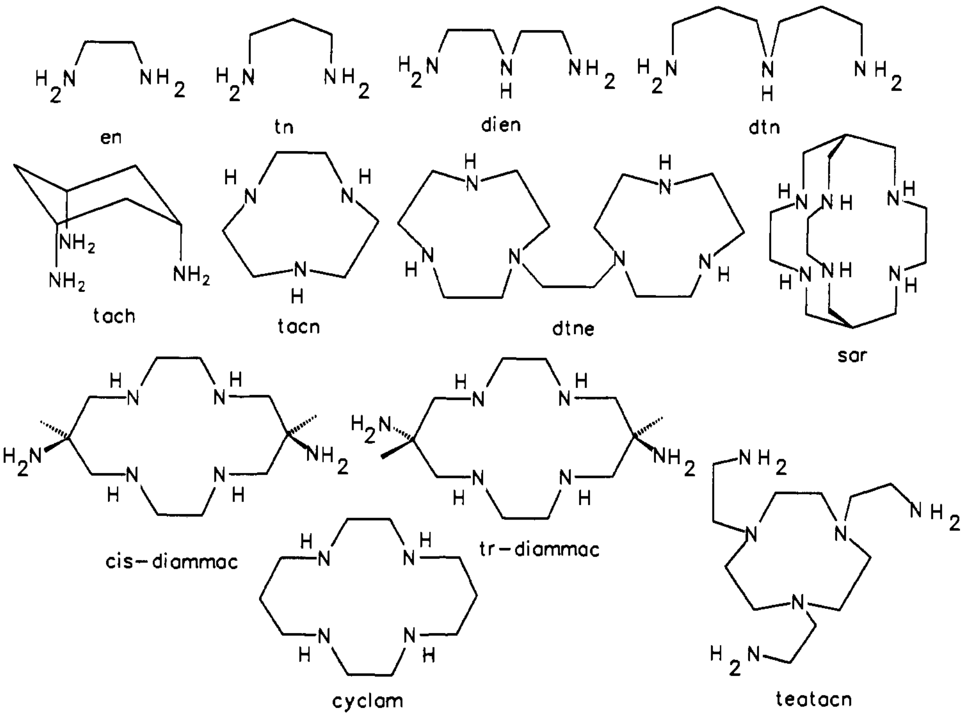
Chart I



Experimental Section

Trial coordinates were generated with the molecular graphics program SMILE[15] or were taken from X-ray crystal structures where available. Molecular mechanics calculations were performed with the strain energy minimization program MOMEC87[16] using a published force field.[8] A slight modification of the force field was made with regard to the Ni(II) hexaamine calculations. Specifically, the strain free Ni–N bond length (r_0) was taken as 2.01 Å, the Ni–N force constant was 0.50 mdyn Å^{-1}, and the van der Waals radius for the N donors was 1.95 Å. This was found to result in a better reproduction of the experimentally determined angular distortions, especially of the trigonal twist angles. Obviously, the energy levels are dependent on the geometry of the entire chromophore, and the angular distortions are included in their computation via AOM calculations. Angular overlap model calculations were performed with a modified version of the program CAMMAG.[17] All pictures were generated with the plotting program ORTEP.[18]

Results

The hexaamine complexes of chromium(III), cobalt(III), and nickel(II) were the systems of choice in order to test the viability of the combination of MM and AOM calculations in a predictive sense. First and foremost, all three systems may be readily modeled within our force field; thus calculation of the geometry of the chromophore is within the scope of the MM calculation. There is also a relatively large volume of spectroscopic data available concerning these complexes, so a wide variety of geometries, and hence ligand field spectra, could be modeled. The absence of π-bonding in the M–N bond of amine complexes immediately eliminates the e_π parameter from all AOM calculations. Furthermore, all systems contain first-row transition metal ions for which spin–orbit coupling is a relatively minor perturbation on the d–d spectra; therefore ζ was set to zero in all cases. The final set of parameters that needed to be held constant were the Condon–Shortley interelectronic repulsion parameters, F_2 and F_4. The variation of these parameters throughout hexaamine complexes is generally modest,[19] so "typical" values were adopted for each system and these are given in Table I. As a consequence of this, the calculated spin-forbidden transitions, which are primarily dependent on F_2 and F_4 but almost insensitive to e_σ, were essentially invariant throughout each series. We have chosen to adopt the relation

$$e_\sigma(r) = C/r^6$$

as the basis for our model; however we do not contend that this relationship is anything other than empirical. Actually, crystal field theory predicts that e_σ should be proportional to r^{-5}.[20] A correction of r for misdirected M–L bonds was not necessary in this case.[7,21]

Table I. Electronic Parameters Used for the AOM Calculations

	Cr(III)	Co(III)	Ni(II)
F_2[a]	1211	1046	1243
F_4[a]	101	85	79
C (NH_3)[b]	583059 (7200)	436543 (7245)	334488 (3582)
C (RNH_2)[b]	599255 (7400)	447882 (7433)	360218 (3857)
C (R_2NH)[b]	647843 (8000)	464890 (7715)	385948 (4133)
C (R_3N)[b]	704530 (8700)	493237 (8186)	428831 (4592)

[a] cm^{-1}. [b] cm^{-1} Å^6; e_σ (cm^{-1}) in parentheses (normalized for Cr^{III}–N = 2.08, Co^{III}–N = 1.98, and Ni^{II}–N = 2.13 Å).

The critical step was to fit values of C such that the predicted spectra, generated from the MM-refined structures, match the experimental spectra. It was found that the C values increase with alkyl substitution for all three systems (Table I). This is chemically reasonable considering the generally accepted view

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(15) Eufri, D.; Sironi, A. *J. Mol. Graphics* **1989**, *7*, 165.

(16) Hambley, T. W. *MOMEC87: A Program for Strain Energy Minimization*; University of Sydney: Sydney, Australia, 1987.

(17) Cruse, D. A.; Davies, J. E.; Gerloch, M.; Harding, J. H.; Mackey, D. J.; McMeeking, R. F. *CAMMAG: A FORTRAN Program*; University of Cambridge: Cambridge, U.K., 1991. Riley, M. J., Universität Bern, Bern, Switzerland, 1992.

(18) Johnson, C. K. *ORTEP: A Thermal Ellipsoid Plotting Program*; Oak Ridge National Laboratory: Oak Ridge, TN, 1965.

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(21) Comba, P.; Hambley, T. W.; Hitchman, M. A.; Stratemeier, H. In preparation.

Table II. Calculated and Experimental Electronic Transitions (cm^{-1}) for Cr(III) Hexaamines (Underscore: Degenerate State)

	$(NH_3)_6$	$(en)_3$	$(tacn)_2$	$(tn)_3$	meso-fac-$(dien)_2$	mer-$(dien)_2$
MM/AOM	21330 28720 21450 28800 21490 28840	21660 28990 $\underline{21840}$ $\underline{29260}$	$\underline{23060}$ 29380 23230 $\underline{31130}$	21180 28230 $\underline{21200}$ $\underline{28700}$	21670 28720 22260 29210 22410 30710	20770 28020 21650 28330 21660 30370
exp.	21640 28940[a]	21800 28490[a]	22780 29400[b]	21570 28190[a]	22170 29070[c]	21700 27850[c]

	mer-$(dtn)_2$	cis-diammac	dtne	teatacn	tr-(cyclam)$(NH_3)_2$	cis-(cyclam)$(NH_3)_2$
MM/AOM	19500 26510 20210 27640 20450 27860	21120 28050 21950 29540 22300 30320	19640 25190 20140 28820 20960 29030	21720 28200 $\underline{22130}$ $\underline{30060}$	22000 28960 22120 30460 24030 31540	21310 28430 21670 28850 21850 29740
exp.	21100 27700[a]	22120 28570[d]	20790 27780[e]	21410 27930[f]	22470 29940[g] 23810	21370 28170[g]

[a] Kühn, K.; Wasgestian, F.; Kupka, H. *J. Phys. Chem.* **1981**, *85*, 665 and references therein. [b] Wieghardt, K.; Schmidt, W.; Herrmann, W.; Küppers, H. *Inorg. Chem.* **1983**, *22*, 2953. [c] Searle, G. H.; House, D. A. *Aust. J. Chem.* **1987**, *40*, 361. [d] Reference 24. [e] Wieghardt, K.; Tolksdorf, I.; Herrmann, W. *Inorg. Chem.* **1985**, *24*, 1230. [f] Perkovic, M. W.; Endicott, J. F. *J. Phys. Chem.* **1990**, *94*, 1217. [g] Kane-Maguire, N. A. P.; Wallace, K. C.; Miller, D. B. *Inorg. Chem.* **1985**, *24*, 597.

Table III. Calculated and Experimental Electronic Transitions (cm^{-1}) for Co(III) Hexaamines (Underscore: Degenerate State)

	$(NH_3)_6$	$(en)_3$	$(tacn)_2$	rac-fac-$(dien)_2$	mer-$(dien)_2$
MM/AOM	21070 29460 21200 29560 21260 29610	$\underline{21470}$ 29690 21600 $\underline{30090}$	21610 29170 $\underline{21770}$ $\underline{30570}$	21030 29220 21320 29750 21390 29880	20920 29160 21430 29340 21450 30550
exp.	21050 29500[a]	21370 29410[a]	21830 30030[a]	21370 29500[b]	21460 29200[b]

	$(tn)_3$	cis-diammac	teatacn	dtne	mer-$(dtn)_2$
MM/AOM	20320 28210 $\underline{20480}$ $\underline{29000}$	21730 29550 22040 30690 22100 30920	20900 28660 $\underline{21320}$ $\underline{30030}$	18460 25880 19100 28470 20470 28700	19080 27190 19140 27740 20020 28070
exp.	20600 28500[a]	21790 29940[c]	20830 28820[d]	20200 28900[e]	19530 27700[a]

[a] Hambley, T. W. *Inorg. Chem.* **1988**, *27*, 2496 and references therein. [b] Kojima, M.; Iwagaki, M.; Yoshikawa, Y.; Fujita, J. *Bull. Chem. Soc. Jpn.* **1977**, *50*, 3216. [c] Reference 24. [d] Hammershøi, A.; Sargeson, A. M. *Inorg. Chem.* **1983**, *22*, 3554. [e] Wieghardt, K.; Tolksdorf, I.; Herrmann, W. *Inorg. Chem.* **1985**, *24*, 1230.

that increasing N-alkylation enhances donor strength. It is worth noting that each *C* value, where possible, was fitted to systems containing six N-donors of one class, i.e. $[M(NH_3)_6]^{n+}$, $[M(en)_3]^{n+}$, $[M(tacn)_2]^{n+}$, etc., so that the *C* values for the different classes were independent of each other. Unfortunately, the *C* values for the tertiary N-donors could not be determined in this way as no complexes containing six tertiary amines could be found. The fitted parameters were then tested by predicting the spectra of mixed amine complexes and the results are given in Tables II–IV. As all systems formally have lower than octahedral symmetry, the calculations reveal splitting of the orbitally degenerate T_1 and T_2 states. However, this splitting was rarely resolved in the corresponding experimental spectrum due to the large line widths (ca. 3000 cm^{-1} at half-height) inherent in room-temperature solution electronic spectra. The results in Tables II-IV, also shown graphically in Figure 1, reveal that the fit between the observed electronic maxima and the "center of gravity" of the predicted envelope of transitions is within 1000 cm^{-1}.

Discussion

General Aspects. In order to genuinely test the combined MM–AOM approach, a wide range of structures was modeled so that the largest possible variation in M–N bond lengths and geometries, was achieved. Previous studies have shown that the *trans*-diammac and meridonal bis(dtn) complexes generally exhibit the strongest ligand field/shortest M–N bond lengths and weakest

Table IV. Calculated and Experimental Electronic Transitions (cm^{-1}) for Ni(II) Hexaamines (Underscore: Degenerate State)

	$(NH_3)_6$	$(en)_3$	$(tacn)_2$	mer-$(dien)_2$	$(tn)_3$	mer-$(dtn)_2$	cis-diammac	dtne	$(tach)_2$
MM/AOM	10680 17090 27740 10730 17140 $\underline{27770}$ 10740 17150	11530 18260 29050 $\underline{11630}$ $\underline{18310}$ $\underline{29300}$	$\underline{12450}$ 18240 $\underline{30020}$ 12570 $\underline{20100}$ 32190	10740 17520 28740 $\underline{11650}$ 17840 28750 18850 29250	10900 17350 $\underline{28040}$ $\underline{17380}$ 28080	10480 16480 27270 10490 17030 27360 10670 17190 27820	11730 18110 29290 12320 19550 30010 12480 19710 31490	10480 15200 27030 10880 18410 27530 11160 18790 29570	$\underline{11630}$ 18140 $\underline{29170}$ $\underline{18430}$ 29470
exp.	10750 17500 28200[a]	11700 18350 29000[a]	12500 19800 30800[a]	11500 18700 29100[b]	10900 17800 28200[b]	10970 17570 28070[b]	12380 18700 30960[c] 20410	10910 19380 27550[d]	11550 18850 29600[e]

[a] Reference 19 and references therein. [b] Lever, A. B. P.; Paoletti, P.; Fabbrizzi, L. *Inorg. Chem.* **1979**, *18*, 1324 and references therein. [c] Reference 24. [d] Wieghardt, K.; Tolksdorf, I.; Herrmann, W. *Inorg. Chem.* **1985**, *24*, 1230. [e] Wentworth, R. A. D. *Inorg. Chem.* **1968**, *7*, 1030.

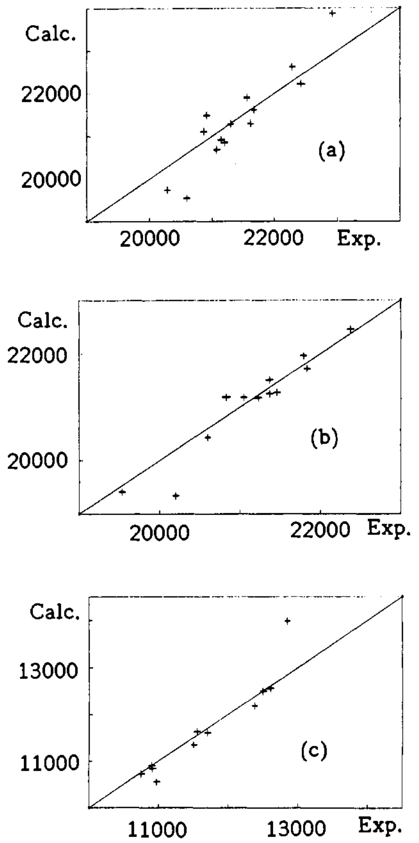

Figure 1. Plot of the experimental versus the calculated lowest energy spin-allowed electronic transitions (cm^{-1}) for hexaamine complexes of (a) Cr(III), (b) Co(III), and (c) Ni(II). The theroretical line of unity slope is also shown.

ligand field/longest M–N bond lengths, respectively, for all hexaamine complexes. Throughout each series of predicted spectra, the variation from the minimum energy ($[M(dtn)_2]^{n+}$) to the maximum energy ([M(*trans*-diammac)]$^{n+}$) for each transition was in the range 3000–4000 cm^{-1}, so significant variations in the predicted transition energies were achieved.

It would be unreasonable to suggest that the combined MM–AOM approach has a strong theoretical base. Both MM and AOM calculations rely on a large number of empirical parameters whose relationship with real physical constants is often nebulous. Furthermore, the functions employed by MM are rather simplistic models of atom–atom interactions. Having said this, it is clear that there are few viable alternatives to empirical approaches such as these at present. *Ab initio* calculations on transition metal complexes,[22] while obviously a more palatable approach, require vast amounts of computer time, and moreover the agreement between predicted and observed electronic transitions is inferior at present to that reported here.

Another important point is that between the first and last stages of the MM–AOM model, i.e. between the trial structure and the predicted electronic transitions, there are two parametrization schemes and errors in both steps might cancel each other out. One way to eliminate the uncertainty introduced in the MM calculation would be to carry out the AOM parametrization solely on solid-state, ideally single-crystal, electronic spectra where the crystal structure was also known. Although this might make the e_σ functions more realistic, the volume of available data is so small that one could not hope to build up a meaningful set of C parameters. It has already been shown that a good fit between the MM-calculated structures and the corresponding crystal structures is achieved using the present force field.[8] Therefore, we anticipate that any errors introduced by the MM calculation will not be critical. Two points that give us confidence in the MM–AOM method are as follows: (a) the increasing trend of the C values with increasing N-alkylation in all three systems makes chemical sense and (b) the fit between the predicted and observed transitions is excellent considering the amount of variables employed in the parametrization and the wide variety of structures and spectra that were modeled.

Specific Examples. [M(*trans*-diammac)]$^{n+}$ and [M(*cis*-diammac)]$^{n+}$. An MM analysis of these macrocyclic hexaamine

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[22] Vanquickenborne, L. G.; Coussens, B.; Postelmans, D.; Ceulemans, A.; Pierloot, K. *Inorg. Chem.* **1991**, *30*, 2978.

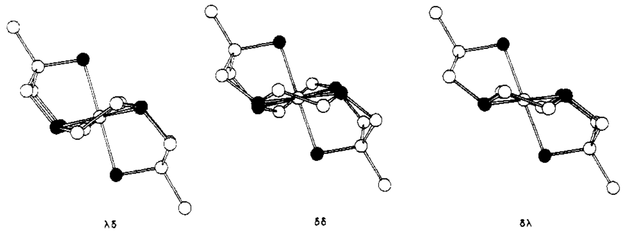

Figure 2. The three nondegenerate conformations of sexidentate coordinated complexes of *trans*-diammac viewed along the C_2 axis.

Table V. Calculated and Experimental Electronic Transitions (cm^{-1}) and Strain-Minimized Energies (kJ mol^{-1}) for $[M($*trans*-diammac$)]^{n+}$ (M = Cr(III), Co(III), Ni(II))

	Cr(III)	Co(III)	Ni(II)
λδ	25630 32750 25710 35170 28240 35250	$\underline{23510}$[a] 31740 24410 32650 32730	14470 21750 34950 14520 23400 35530 16380 23450 36030
Strain Energy	87.94	99.15	123.78
δδ	23320 30620 23730 32230 26070 33410	22060 30150 22280 30720 23020 31870	13330 20240 32280 13500 21370 33810 15110 22740 34220
Strain Energy	79.25	101.75	115.97
δλ	20560 27820 21530 28780 23330 31590	19930 27690 20340 28060 21140 30750	11750 17880 28610 12150 18490 31050 12850 21590 31680
Strain Energy	88.71	128.60	125.64
exp.	23420 30120[b]	22370 30490[c]	12530 13160 20500 31970[d]

[a] Accidentally degenerate state. [b] Bernhardt, P. V.; Comba, P.; Curtis, N. F.; Hambley, T. W.; Lawrance, G. A.; Maeder, M.; Siriwardena, A. *Inorg. Chem.* **1990**, *29*, 3208. [c] Bernhardt, P. V.; Hambley, T. W.; Lawrance, G. A. *J. Chem. Soc., Dalton Trans.* **1989**, 1059. [d] Reference 24.

complexes revealed that there are three nondegenerate conformations of both the *trans* and *cis* isomers.[23] The calculations showed that one particular conformation of $[M($*cis*-diammac$)]^{n+}$ (denoted λλ) is always more stable than the other two, regardless of the metal ion size. Indeed this conformation has been identified in the two extant crystal structures of complexes containing this ligand;[24,25] therefore this conformer was the only one considered in the present study. On the other hand, the three conformations of sexidentate coordinated complexes of *trans*-diammac (Figure 2) show distinct preferences for metal ions of various sizes.[23] It was shown that the most stable conformation changes from λδ to δδ to δλ as the metal ion size increases. An analysis of the predicted spectra of each conformation of the Co(III), Cr(III), and Ni(II) complexes of *trans*-diammac is presented in Table V. In all cases, the δδ conformer yields the electronic transitions most consistent with the experimental spectrum. This is essentially consistent with MM predictions based on the strain-minimized energies, except for the Co(III) system, where the λδ conformer was predicted to be 2.6 kJ/mol more stable than the δδ conformer; however such an energy difference is small on the energy scale of molecular mechanics calculations.

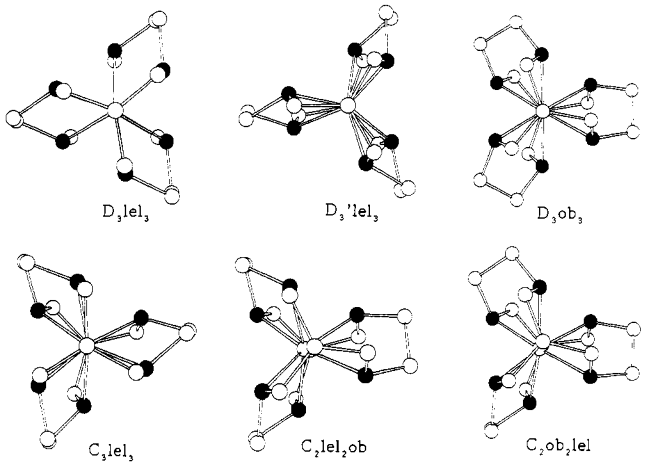

Figure 3. The six nondegenerate conformations of $[M(sar)]^{n+}$ complexes viewed along the apical C atom–M axis. The lel and ob nomenclature refers to the ethylene group in the five-membered chelate ring being parallel or oblique, respectively, to this axis.

Table VI. Calculated and Experimental Electronic Transitions (cm^{-1}) and Strain-Minimized Energies (kJ mol^{-1}) for $[M(sar)]^{n+}$ Complexes (Underscore: Degenerate State)

	Cr(III)	Co(III)	Ni(II)
D_3lel_3	23570 30950 $\underline{23740}$ $\underline{31310}$	21730 30130 $\underline{21780}$ $\underline{30180}$	12250 18830 $\underline{30450}$ $\underline{12410}$ $\underline{19530}$ 30640
Strain Energy	90.61	128.17	122.48
D_3ob_3	$\underline{25440}$ $\underline{32720}$ 25520 33660	22560 30810 $\underline{22690}$ $\underline{31560}$	$\underline{14050}$ $\underline{21110}$ 32860 14090 22110 $\underline{33790}$
Strain Energy	101.76	128.84	141.60
C_3lel_3	23030 30290 $\underline{23310}$ $\underline{30910}$	21020 29200 $\underline{21240}$ $\underline{29700}$	12480 19270 30900 $\underline{12630}$ $\underline{19740}$
Strain Energy	87.13	126.81	120.73
C_2lel_2ob	21940 29190 22420 29540 22850 30850	20200 28830 20260 29450 20670 30430	12140 18540 29990 12200 19100 30270 12450 19920 30830
Strain Energy	85.68	126.89	121.10
C_2ob_2lel	23790 30740 23870 31580 24060 31920	21090 29800 21140 30600 21320 30920	13020 19700 31300 13110 20440 31880 13290 20740 32410
Strain Energy	91.53	126.18	129.57
exp.	21860 22250 28820[a]	21230 29150[b]	12390 19760 12820 20410 30300[c]

[a] Comba, P.; Creaser, I. I.; Gahan, L. R.; Harrowfield, J. M.; Lawrance, G. A.; Martin, L. L.; Mau, A. W. H.; Sargeson, A. M.; Sasse, W. H. F.; Snow, M. R. *Inorg. Chem.* **1986**, *25*, 384. [b] Geue, R. J.; Hambley, T. W.; Harrowfield, J. M.; Sargeson, A. M.; Snow, M. R. *J. Am. Chem. Soc.* **1984**, *106*, 5478. [c] Comba, P.; Sargeson, A. M. Unpublished work.

$[M(sar)]^{n+}$. It has been shown that there are six important conformations of the macrobicyclic hexaamine sar (Figure 3).[26] Strain energy minimization of the Co(III), Cr(III), and Ni(II) complexes was performed, and the relevant structural data are given in Table VI, together with the predicted electronic transitions. The trigonally twisted $D_3'lel_3$ conformer was found to be quite unstable relative to the remaining conformers, and therefore it will not be discussed further. A significant variation in the predicted electronic spectra was identified throughout the series of conformers. The C_2lel_2ob conformer of $[Cr(sar)]^{3+}$ yielded a spectrum consistent with that found in solution, and this conformation also possessed the lowest strain-minimized energy. The D_3lel_3, C_3lel_3, and C_2lel_2ob conformers of $[Ni(sar)]^{2+}$ all possessed similar strain-minimized energies, and all yielded spectra consistent with those found in solution. The range of minimized strain energies for the five stable conformations of $[Co(sar)]^{3+}$ was less than 3 kJ/mol; however the three most stable conformers (C_3lel_3, C_2lel_2ob, and C_2ob_2lel) all gave spectra that were similar to the experimental solution spectrum.

A similar analysis was performed on the four conformers of $[M(en)_3]^{n+}$, namely D_3lel_3, C_2lel_2ob, C_2ob_2lel, and D_3ob_3; however the variation in geometries and strain energies was barely

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(23) Bernhardt, P. V.; Comba, P. *Helv. Chim. Acta* **1991**, *74*, 1834; **1992**, *75*, 645.
(24) Bernhardt, P. V.; Comba, P.; Hambley, T. W.; Lawrance, G. A.; Várnagy, K. *J. Chem. Soc., Dalton Trans.* **1992**, 355.
(25) Bernhardt, P. V.; Comba, P.; Hambley, T. W. *Inorg. Chem.*, in press.
(26) Comba, P. *Inorg. Chem.* **1989**, *28*, 426.

significant throughout the series, and the variation in the predicted electronic transitions was less than ±200 cm^{-1}.

Conclusions

We believe that the results presented herein demonstrate that one can predict quite accurately the d–d electronic transitions of Co(III), Cr(III), and Ni(II) hexaamine complexes using the combination of molecular mechanics and angular overlap model calculations. It was important to ensure that errors introduced in the two parametrization schemes did not cancel each other out, which emphasizes the importance of employing a wide as possible range of geometries for the chromophores under scrutiny.

The transferability of AOM parameters was a vital factor enabling the MM–AOM method to be used in a predictive role. Considering the variety of geometries and spectra modeled in this work, the fit obtained between experimental and predicted transitions shows that such a role for the AOM is not one to be ignored. The progressive increase in the C values for all three systems is consistent with the popular view that N-alkylation increases donor strength. Direct evidence for this trend has been rare, as steric and electronic effects often oppose one another. This is particularly relevant for complexes of tertiary amines where weaker ligand fields are generally observed than for secondary amines. The results presented herein indicate that the tertiary amines are indeed stronger donors (larger C values); however steric effects generally dictate that the M–NR_3 bond is sufficiently elongated that the e_σ value is less than that found in typical secondary amine complexes.

Expansion of these systems to the prediction of electronic properties of other types of coordination compounds is the next task to be undertaken. Predictive structural and spectroscopic transition metal coordination chemistry is still a relatively unexplored field, and there are many areas in which the MM–AOM method might find application. Specific examples include the design of complexes with particular electronic properties and the determination of solution structures. The development of new and improved force fields that will be able to deal with classes of compounds yet to be modeled with MM must also accompany this work. Finally, it is important that the pursuit of predictive spectroscopic studies based on AOM and related ligand field models be continued in order that strong links are established and maintained between MM results and solution behavior of these systems.

Acknowledgment. We gratefully acknowledge financial support from the Swiss National Science Foundation (Grant No. 20-28522.90), and we thank Dr. M. J. Riley for supplying us with his modified version of the CAMMAG program.