Inorg. Chem. **2002**, *41*, 2660–2666

Inorganic Chemistry
Article

Statistical and Molecular Mechanics Analysis of the Effects of Changing Donor Type on Bond Length in the Two Series $[\mathrm{Co^{III}N}_n\mathrm{O}_{6-n}]$ and $[\mathrm{Ni^{II}N}_n\mathrm{O}_{6-n}]$ ($n = 0$–6): A New Route to Bond-Stretch Parameters

Rosalie K. Hocking and Trevor W. Hambley*

Centre for Heavy Metals Research, School of Chemistry, University of Sydney,
Sydney, NSW 2006, Australia

Received August 28, 2001

Changes in bond lengths across the series of complexes $[\mathrm{Co^{III}N}_n\mathrm{O}_{6-n}]$ and $[\mathrm{Ni^{II}N}_n\mathrm{O}_{6-n}]$, ($n = 0$–6) have been examined by a statistical analysis of the bond lengths in 256 $\mathrm{Co^{III}}$ and 205 $\mathrm{Ni^{II}}$ complexes. In both cases a systematic reduction in both metal-N and metal-O bond lengths is observed as oxygen donors replace nitrogen in the coordination sphere. In the case of $\mathrm{Co^{III}}$, the reduction in bond lengths is linear across the series, whereas, in the case of $\mathrm{Ni^{II}}$, it is more asymptotic in nature. It was found that this systematic change to the inner coordination sphere produced a much larger range of bond lengths than had previously been observed by changes to the outer sphere. The trends across the two series were reproduced using molecular mechanics; however, the magnitude of the change was not initially predicted correctly in either case. Alterations to molecular mechanics parameters that reproduced the trends in the $[\mathrm{Co^{III}N}_n\mathrm{O}_{6-n}]$ series also resulted in a significant overall improvement in the predictions of $\mathrm{Co^{III}}$–N bond lengths in a series of $\mathrm{Co^{III}}$ hexaamines, with all being reproduced within 0.006 Å. This improvement was taken as an indication that the bond-length reduction across the series is largely steric in origin.

Introduction

Ligands within a complex can have a profound effect on the behavior of other ligands in the same complex. The most well-known of these are the trans-effects in complexes such as square-planar platinum(II).[1] Interligand effects can be electronic or steric in origin. Steric effects are a consequence of the size and positioning of the donor atoms, whereas electronic effects are characterized by an electronic interdependence of different donor types.[2,3] To some extent, molecular mechanics (MM) can be used to separate the electronic effects from the steric effects, as it can be used to predict the size and position of atoms. This has been utilized in many useful ways and has a proven predictive power, particularly in the case of the $\mathrm{Co^{III}}$ hexaamines where the reduction potentials and electron-transfer properties of the series have been reproduced.[4,5] In contrast, electronic effects such as the elongation of the Co−$\mathrm{NH_3}$ bond trans to the $\mathrm{CH_3}$ in $[\mathrm{Co(NH_3)_5CH_3}]^{2+}$ cannot be reproduced using traditional MM.[6,7] Such effects would be characterized by a shift in the ideal bond length of a metal−ligand interaction, which cannot be accounted for by a single set of metal−ligand stretch parameters.[2,4,5,8]

Complexes with oxygen and nitrogen donors are probably the most widely studied in coordination chemistry. This has meant that over the years a wealth of data has been accumulated on their properties from kinetic substitution effects[9] to the large number of crystal structures reported containing only oxygen and nitrogen donor groups. For example, of the 8391 cobalt-containing structures reported to the CSD,[10−12] 4400 have at least one cobalt−nitrogen (Co−N) bond and 2546 have at least one Co−O bond.

---

* To whom correspondence should be addressed. Phone: 61-2-9351-2830. Fax: 61-2-9351-3329. E-mail: t.hambley@chem.usyd.edu.au.

(1) Orgel, L. E. *Inorg. Nucl. Chem.* **1956**, *2*, 137−140.
(2) Comba, P.; Hambley, T. W. *Molecular Modelling of Inorganic Compounds*; 2nd ed.; Wiley−VCH: New York, 2001.
(3) Comba, P. In *Molecular Mechanics Modelling of Transition Metal Compounds*; Howard, J. A. K., Ed.; NATO Science Series, Series E; Kluwer: Dordrecht, The Netherlands, 1999; Vol. 360, pp 71−86.
(4) Hambley, T. W. *Inorg. Chem.* **1988**, *27*, 2496−2501.
(5) Comba, P.; Sickmuller, A. F. *Inorg. Chem.* **1997**, *36*, 4500−4507.
(6) Kofod, P.; Harris, P.; Larson S. *Inorg. Chem.* **1997**, *36*, 2258−2266.
(7) Hocking, R. K.; Hibbs, D. E.; Hambley, T. W. Unpublished results.
(8) Comba, P. *Coord. Chem. Rev.* **1998**, *182*, 343−371.
(9) Margerum, D. W.; Cayley, G. R.; Weatherburn, D. C.; Pagenkopf, G. K. In *Kinetics and Mechanism of Complex Formation and Ligand Exchange*; Martell, A. E., Ed.; ACS Monograph Series; American Chemical Society: Washington, D.C., 1978; pp 1−220.
(10) The Cambridge Structural Database, www.ccdc.cam.ac.uk, 2001.
(11) Allen, F. H.; Kennard, O. *Chem. Des. Autom. News.* **1993**, *8*, 31−37.
(12) Allen, F. H. *Trans. Am. Crystallogr. Assoc.* **2000**, *32*, 1−5.

10.1021/ic010930z CCC: $22.00

There have been some recent successes in the extraction of information from the large set of data held in the CSD,[13] including analysis by valence bond sums[14] and some novel types of conformational analysis.[15-18] Here we use structural data reported to the CSD to perform a statistical analysis of bond lengths across the two series of complexes containing only oxygen and nitrogen donors: $[Ni^{II}N_nO_{6-n}]$ and $[Co^{III}N_nO_{6-n}]$ ($n = 0-6$). The observed trends in bond lengths have been investigated using MM to establish their origin. In the process, we have found a new way of determining MM parameters describing metal−ligand interactions.

Experimental Section

Statistical Analysis. Structures that fulfilled the criteria defining donor types outlined below, were extracted from the Cambridge Structural Database (CSD,[11,13] Version 5.18) and the average lengths of M−N and M−O (M = Co^{III} and Ni^{II}) bonds were recorded for each set of complexes, $[Co^{III}N_nO_{6-n}]$ and $[Ni^{II}N_nO_{6-n}]$ ($n = 0-6$). Structures reported before 1979 and structures with R-values > 7.5 were excluded with a few exceptions.

All nitrogen donors considered were simple am(m)ines. Donors were permitted to be primary, secondary or tertiary amines or ammonia, but donors were not allowed to be a component of an aromatic ring or be attached directly or within one donor to a group other than carbon or hydrogen. Oxygen donors were allowed to originate from carbonate, water, hydroxide, oxalate, carboxylate, or similar derivatives. Donors connected directly to groups other than carbon or hydrogen were excluded; bridged oxygen donors were permitted provided they bridged two identical metal centers and comprised less than half the bonding in any particular complex.

Each series was analyzed to give a mean, median, standard deviation, and confidence interval for each value of n. Confidence intervals (CI) were calculated using the formula $CI = \alpha(\sigma N^{-1/2})$, where σ is the standard deviation and N is the number of structures in the sample. The α value reflects the size of the confidence interval; in this paper 95% confidence intervals are quoted on the mean, which corresponds to an α-value of 1.96.[19,20] Histograms showing the spread of the data are available with the Supporting Information (Figures S5 and S6).

In the cases of $[Co^{III}N_4O_2]$, $[Ni^{II}N_4O_2]$, and $[Ni^{II}N_2O_4]$ a further subset of each group was analyzed. In the cases of $[Co^{III}N_4O_2]$ and $[Ni^{II}N_4O_2]$, the subsets with cis and trans oxygen donors were analyzed, and in the case of $[Ni^{II}N_2O_4]$, the two subsets with cis and trans nitrogen donors were analyzed. In the subset of *cis*-$[Co^{III}N_4O_2]$, a further division was made into "Co^{III}−N bonds cis to oxygen" and "Co^{III}-N bonds trans to oxygen", and these were analyzed in the manner used for the other data sets. Within the resolution of analysis no structural trans influences were found. These data are included with the Supporting Information (Figures S14−S17).

Table 1. Published Molecular Mechanics Parameters of Relevance to This Study

	ϵ /k_b (mdyn/Å)	r_0/r_{vdw} (Å)	ref no.
O (nonbonded)	0.055	1.7	22,23
N (nonbonded	0.05	1.8	22,23
Ni^{II}−N (bond stretch)	0.60	2.06	22,23
Co^{III}-N (bond stretch)	1.75	1.905	22,23
Co^{III}-O (bond stretch)	1.75	1.845	24

Molecular Mechanics. Molecular mechanics (MM) calculations were performed using the commercially available software, MOMEC97,[2,21] using a published force field, unless otherwise stated (Table 1).[22,23]

From each of the larger data sets a subset of approximately five structures was chosen for MM analysis of each point (value of n). These data were used to determine whether optimizing the ϵ and r_{vdw} values for the O and N atoms improved fits between experimental and MM calculated trends. Similarly, the parameters r_0 and k_b were adjusted until the curves produced by the force-field overlayed the curves that were derived statistically. All minimizations were carried out in MOMEC97 until the convergence criteria of a shift < 0.01 Å for Ni^{II} and < 0.001 Å for Co^{III} were achieved.

Those structures used in the "full set" and "subset" analyses are recorded using their CSD names in Appendix 1 of the supporting information. The subset analyses included the following structures: $[Co(en)_3]^{3+}$, $[Co(NH_3)_6]^{3+}$, $[Co(acac)_3]^{3+}$, $[Co(ox)_3]^{3+}$, $[Ni(H_2O)_6]^{2+}$, and $[Ni(en)_3]^{2+}$ for which three or more structures had been reported to the CSD. Those structures for each complex with an R-value < 7.5% were averaged, and the confidence interval calculated on the mean. This was done in place of quoting the bond lengths of a single structure in each case. The structures used and the confidence intervals calculated are recorded in the Supporting Information.

Results and Discussion

Statistical Analysis. The objective of this study was to determine whether a systematic variation in donor types could cause an observable structural change. It was anticipated that if such effects existed, they would be quite small. If this was the case, then any lengthening or shortening of bonds due to a change in donor type could not be readily identified in individual structures because of other effects such as differing steric bulk of the ligand hydrogen bonding and crystal packing.

Use of a sufficiently large data set can "average out" random effects that are common to all data points across a series. This type of multivariate analysis is common to disciplines of social science and psychology,[25,26] and it is only in recent years that chemists have had sufficient crystallographic data for analogous analyses.[15,16] In the data sets studied here the randomness arises from both crystallographic effects and different coordination environments.

---

(13) Allen, F. H.; Davies, J. E.; Galloy, J. J.; Johnson, O.; Kennard, O.; Macrae, C. F.; Mitchell, E. M.; Mitchell, G. F.; Smith, J. M.; Watson, D. G. *J. Chem. Inf. Comput. Sci.* **1991**, *31*, 187−204.

(14) Thorp, H. H. *Inorg. Chem.* **1998**, *37*, 5690−5692.

(15) Zimmer, M. *Coord. Chem. Rev.* **2001**, *212*, 133−163.

(16) Fatima, M.; Zimmer, M. *Inorg. Chem.* **1996**, *35*, 2872−2877.

(17) Allen, F. H.; Pitchford, N. A. *Structure-Based Drug Design; NATO ASI Series, Series E*; Kluwer: Dordrecht, The Netherlands, 1998; Vol. 352, pp 15−26.

(18) Yao, J. W.; Copley, R. C. B.; Howard, J. A. K.; Allen, F. H.; Motherwell, W. D. S. *Acta Crystallogr.* **2001**, *B57*, 251−260.

(19) Phipps, M. C.; Quine, M. P. *A Primer of Statistics: Data Analysis, Probability, Inference*; Prentice Hall: Sydney, Australia, 1995.

(20) Spiegel, M. R. *Probability and Statistics*; McGraw-Hill: London, 1975.

(21) Comba, P.; Hambley, T. W.; Okon, N. *MOMEC, a Molecular Modeling Package for Inorganic Compounds*; Laurer & Okon: Heidelberg, Germany, 1995.

(22) Bernhardt, P. V.; Comba, P. *Inorg. Chem.* **1992**, *31*, 2638−2644.

(23) Comba, P.; Hambley, T. W.; Stroehle, M. *Helv. Chim. Acta* **1995**, *78*, 2042−2047.

(24) Hambley, T. W. *Acta Crystallogr.* **1988**, *B44*, 601−609.

(25) Harris, R. J. *A Primer of Multivariate Statistics*; Academic Press: New York, 1985.

(26) Fox, J. *Linear Statistical Models and Related Methods with Applications to Social Research*; Wiley: New York, 1984.

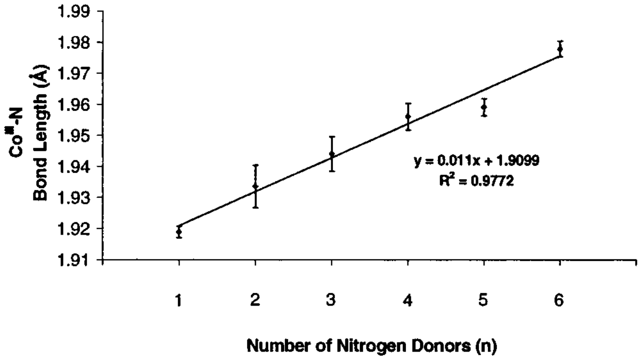

Figure 1. Average $Co^{III}-N$ bond lengths as a function of *n* in the $[Co^{III}N_nO_{6-n}]$ series of complexes. Error bars indicate a 95% confidence interval on the average bond length.

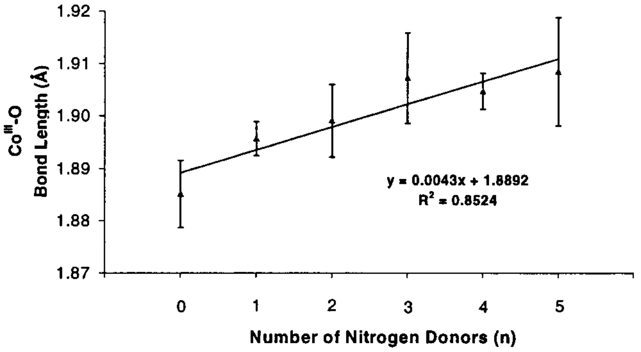

Figure 2. Average $Co^{III}-O$ bond lengths as a function of *n* in the $[Co^{III}N_nO_{6-n}]$ series of complexes. Error bars indicate a 95% confidence interval on the average bond length.

A series of seven different sets of cobalt and nickel complexes with different numbers of oxygen and nitrogen donors in the coordination sphere were analyzed, i.e., the series of complexes $[Co^{III}N_nO_{6-n}]$, and $[Ni^{II}N_nO_{6-n}]$, ($n = 0-6$). The respective Co^{III} and Ni^{II} series were chosen for two reasons: first, the large number of structures reported to the CSD for each metal and, second, both Co^{III} (low spin) and Ni^{II} (high spin) have O_h symmetry. The high symmetry of these species means that the analyses are not complicated by Jahn−Teller[27,28] distortions, or any other deviation from octahedral symmetry that is electronic in origin.

In addition to selecting the metal centers carefully, it was ensured that the nitrogen donor groups used in each series were electronically similar. For this reason only "electronically naïve" amine groups where the nitrogen was sp^3 hybridized were chosen to represent "N", whereas sp^2 hybridized groups, such as pyridine, were excluded to minimize the complications of π-bonding and electron delocalization effects. Amine groups that were coordinated to donors other than carbon or hydrogen, (e.g., NH_2OH) were also excluded because they were considered to be too different electronically from a simple amine.

sp^2 and sp^3 hybridized oxygen donors were included in the one data set since MM analysis shows that the differences between the two types of donor groups are primarily steric in origin (Figure S10 of the Supporting Information). By combining the two groups we have a more statistically significant data set, which we can then deal with in a straightforward way.

Figures 1−4 and Tables 2−5 show the systematic variation in bond lengths observed as the set of donor types is changed from N_6 to O_6. It emerges that a statistically significant decrease (up to 0.12 Å) in both the M−N and M−O bond lengths occurs as the number of oxygen donors is increased. In the case of Co^{III} the decrease is linear in nature, whereas in the case of Ni^{II} the decrease appears to be asymptotic. Each point in the plots represents a large set of structures and has a large standard deviation relative to the magnitude of change across the series. In this situation, confidence intervals are a more appropriate indicator of statistical significance because they are based on the uncertainty in the mean and not the distribution of the data set; as a data set gets larger, the uncertainty in its mean decreases (Tables 2−5).

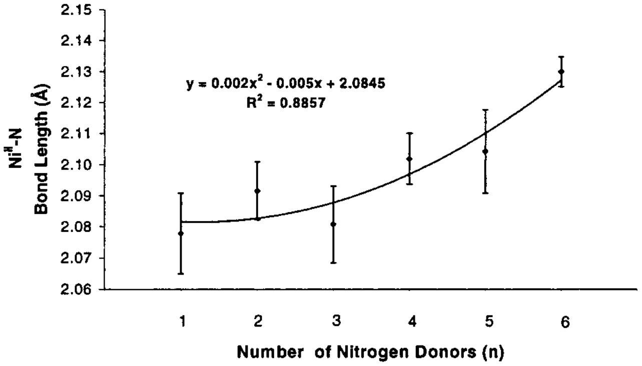

Figure 3. Average $Ni^{II}-N$ bond lengths as a function of *n* in the $[Ni^{II}N_nO_{6-n}]$ series of complexes. Error bars indicate a 95% confidence interval on the average bond length.

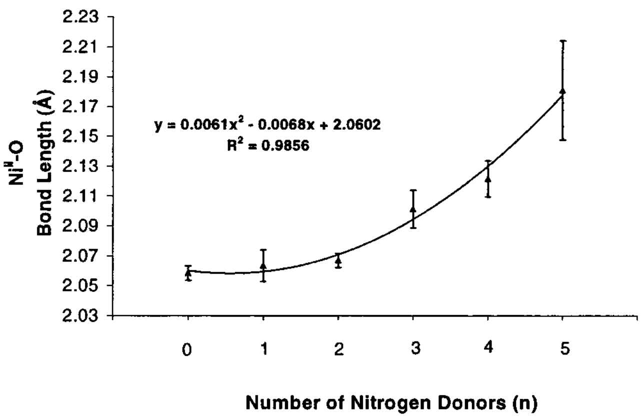

Figure 4. Average $Ni^{II}-O$ bond lengths as a function of *n* in the $[Ni^{II}N_nO_{6-n}]$ series of complexes. Error bars indicate a 95% confidence interval on the average bond length.

The relative degree of uncertainty in the $Co^{III}-O$ and $Ni^{II}-N$ series is larger than for the corresponding $Co^{III}-N$ and $Ni^{II}-O$ series, because of the smaller change across each series. The $Co^{III}-N$ and the $Ni^{II}-O$ bond lengths vary the most across their respective series, and therefore, the error relative to the magnitude of change is less (Tables 2−5).

In any type of statistical analysis there is the possibility that the data set is biased. For both the Ni^{II} and Co^{III} series, the majority of structures reported to the CSD contain

---

(27) Jahn, H. A.; Teller, E. *Proc. R. Soc. London, Ser. A* **1937**, *161*.
(28) Jahn, H. A. *Proc. R. Soc. London, Ser. A* **1938**, *164*.

Table 2. Statistical Data on Co^{III}-N Bond Lengths (Å) in the Series of $[Co^{III}N_nO_{6-n}]$ complexes

no. of nitrogen donors	mean $Co^{III}-N$ (Å)	median $Co^{III}-N$ (Å)	std dev	no. of structures	confidence interval (95%)
1	1.919	1.920	0.002	4	0.0018
2	1.934	1.928	0.020	25	0.0087
3	1.944	1.944	0.011	16	0.0056
4	1.956	1.954	0.013	78	0.0043
5	1.960	1.957	0.014	55	0.0026
6	1.978	1.970	0.017	60	0.0025
range/sum	0.057	0.050		238	

Table 3. Statistical Data on $Co^{III}-O$ Bond Lengths (Å) in the Series of $[Co^{III}N_nO_{6-n}]$ Complexes

no. of oxygen donors	mean Co^{III}-O (Å)	median Co^{III}-O (Å)	std dev	no. of structures	confidence interval (95%)
6	1.885	1.880	0.012	13	0.0064
5	1.896	1.896	0.003	4	0.0032
4	1.899	1.901	0.040	25	0.0062
3	1.907	1.903	0.018	16	0.0087
2	1.905	1.906	0.016	78	0.0034
1	1.908	1.907	0.039	55	0.010
range/sum	0.023	0.027		191	

Table 4. Statistical Data on $Ni^{II}-N$ Bond Lengths (Å) in the Series of $[Ni^{II}N_nO_{6-n}]$ Complexes

no. of nitrogen donors	mean Ni^{II}-N (Å)	median Ni^{II}-N (Å)	std dev	no. of structures	confidence interval (95%)
1	2.078	2.074	0.019	8	0.013
2	2.092	2.082	0.032	44	0.009
3	2.081	2.082	0.030	23	0.012
4	2.102	2.093	0.032	57	0.008
5	2.104	2.106	0.015	5	0.013
6	2.130	2.129	0.015	39[a]	0.005
range/sum	0.052	0.045		176	

[a] Due to the size of this data set, only structures with CSD names beginning with A−M were included.

Table 5. Statistical Data on $Ni^{II}-O$ Bond Lengths (Å) in the Series of $[Ni^{II}N_nO_{6-n}]$ Complexes

no. of oxygen donors	mean Ni^{II}-O(Å)	median Ni^{II}-O (Å)	std dev	no. of structures	confidence interval (95%)
6	2.058	2.059	0.014	29[a]	0.0048
5	2.063	2.063	0.015	8	0.0105
4	2.067	2.067	0.016	44	0.0047
3	2.101	2.107	0.031	22	0.0127
2	2.122	2.127	0.048	58	0.0122
1	2.181	2.167	0.038	5	0.0333
range/sum	0.123	0.108		163	

[a] Due to the size of this data set, only structures with CSD names beginning with A−H were included.

chelating groups, and many common ligands (eg., EDTA, en, acac, H_2O) reappear throughout each series. For example, of the 55 structures reported for the $[Co^{III}N_5O]$ data point, 50 contain glycine. Therefore, the MM analysis described below was performed on a representative subset of the larger data set.

Molecular Mechanics Analysis

$[Co^{III}N_nO_{6-n}]$ Series. To investigate the cause of the decrease in bond lengths with increasing *n* across the $[Co^{III}N_nO_{6-n}]$ and $[Ni^{II}N_nO_{6-n}]$ series, subsets of the larger data sets were examined using MM. MM methods were primarily applied to establish whether the bond shortening effect was "steric" or "electronic" in origin. A steric effect would be reproduced by MM, whereas an electronic effect would be characterized by the need for distinct sets of metal−ligand parameters, depending on the other ligands present in the coordination sphere.[29,30]

It was found using published MM parameters[22,31,32] that a bond shortening was observed across the two series. This indicates that the experimentally observed decrease in bond lengths is, at least in part, due to steric effects. However, the magnitude of the effect was not predicted correctly using MM. This is illustrated for the $[Co^{III}N_nO_{6-n}]$ series in Figure 5; the gradient of the line representing the bond lengths calculated with the previously reported MM parameters is lower than that representing the bond lengths derived by statistical analysis.

To establish whether the underestimate of the trend was indicative of an electronic interrelationship between M−N and M−O bonds or an inadequacy in the current MM parameters, the force field was examined in order to establish whether it could be adjusted to reproduce the trend. Metal−ligand bond lengths are the result of a counterplay between the steric repulsions between adjacent donors (1,3-interactions) and the bond stretch function, which describes the metal−ligand interaction (Figure S7 of the Supporting Information). No alterations to the 1,3 interactions were able to produce the magnitude of the trend correctly (Figure S8 of the Supporting Information). Consequently, the bond stretch parameters describing $Co^{III}-N$ and $Co^{III}-O$ interactions, k_b and r_0, were optimized against the series, keeping nonbonded parameters at the previously reported values (Table 1). We found that this optimization process (to a good approximation) resulted in linearly independent solutions in k_b and r_0 with values derived for the $Co^{III}-N$ interaction

---

(29) Deeth, R. J.; Munslow, I. J.; Paget, V. J. *NATO ASI Ser.* **1997**, *3*, 77−103.

(30) Burton, V. J.; Deeth, R. J.; Kemp, C. M.; Gilbert, P. J. *J. Am. Chem. Soc.* **1995**, *117*, 8407−8415.

(31) Snow, M. R. *J. Am. Chem. Soc.* **1970**, *92*, 3610−3617.

(32) Brubaker, G. R.; Johnson, D. W. *Inorg. Chem.* **1983**, *22*, 1422−1426.

(33) Brunner, H.; Ludi, A.; Raselli, A.; Burgi, H.-B. *Helv. Chim. Acta* **1996**, *79*, 1607−1610.

(34) Yoneda, H. Unpublished data.

(35) Henrick, K.; McPartlin, M.; Munjoma, S.; Owston, P. G.; Peters, R.; Sangokoya, S. A.; Tasker, P. A. *J. Chem. Soc., Dalton Trans.* **1982**, *225−227*.

(36) Bernhardt, P. V.; Lawrence, G. A.; Hambley, T. W. *J. Chem. Soc., Dalton Trans.* **1989**, *1059−1065*.

(37) Bernhardt, P. V.; Jones, L. A. *J. Chem. Soc., Dalton Trans* **1998**, 1757−1761.

(38) Hambley, T. W.; Searle, G. H.; Snow, M. R. *Aust. J. Chem.* **1982**, *35*, 1285−1295.

(39) Ishi, M.; Umehara, M.; Harada, K.; Nakahara, M. *Bull. Chem. Soc. Jpn.* **1987**, *60*, 2683−2685.

(40) Hummel, H. U.; Beiler, F. *Z. Anorg. Allg. Chem.* **1988**, *565*, 147−153.

(41) Vezzosi, I. M.; Benedetti, A.; Saladini, M.; Battaglia, L. P.; Corradi, A. B. *Inorg. Chim. Acta* **1985**, *97*, 195−199.

(42) Kristiansson, O. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1999**, *55*, IUC9900036.

(43) Hynes, R. C.; Willis, C. J.; Vittal, J. J. *Acta Crystallogr., Sect C: Cryst. Struct. Commun.* **1996**, *52*, 1872−1881.

(44) Zompa, L. J.; Margulis, T. N. *Inorg. Chim. Acta* **1980**, *45*, L263−L264.

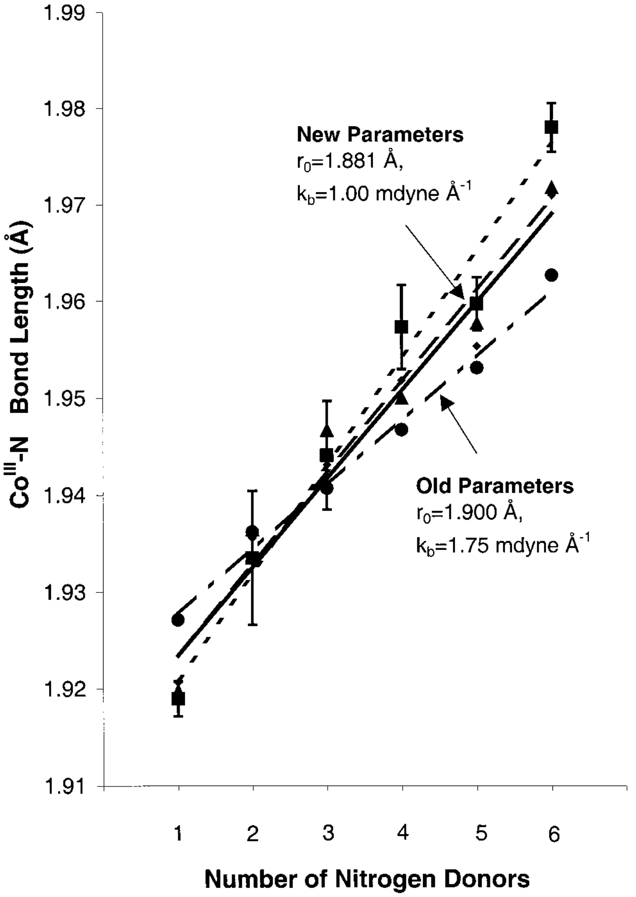

Figure 5. Comparison of molecular mechanics results with statistical analysis for the Co^{III}−N bond lengths of the $[Co^{III}N_nO_{6-n}]$ series. In each case the lines represent a line of best fit through the series and the error bars a 95% confidence interval on the mean. Full data analysis for the subset and the molecular mechanics optimized subset is available with the Supporting Information for this paper. (−■−) Full statistical analysis as illustrated in Figure 1. (−▲−) Subset analysis: The average bond lengths of the subset of structures given in Appendix 1 (Supporting Information). (--◆--) Molecular-mechanics optimized subset: The subset of structures optimized with the molecular mechanics parameters, r_0 = 1.881 Å and k_b = 1.00 mdyn Å^{-1}. (●) Molecular mechanics optimized subset with old parameters k_b = 1.75 mdyn Å^{-1} and r_0 =1.905 Å. [22,23]

being $k_b = 1.0$ mdyn Å^{-1} and $r_0 = 1.881$ Å and for Co^{III}−O $k_b = 1.005$ mdyn Å^{-1} and $r_0 = 1.856$ Å (Co^{III}−N, Figure 5; Co^{III}−O, Figure S11 of the Supporting Information).

Table 6. Comparison of Molecular Mechanics Results with New Parameters Derived from the $[Co^{III}N_nO_{6-n}]$ Series Compared with Those Reported Previously for the Hexamine Complexes

compound	exptl	old param[2] ($k = 1.75$ mdyn Å^{-1}, $r_0 = 1.905$ Å)	new param ($k = 1.00$ mdyn Å^{-1}, $r_0 = 1.881$ Å)
$[Co(NH_3)_6]^{3+}$ [a]	1.963	1.955	1.964
$[Co(en)_3]^{3+}$	1.961	1.963	1.965
$[Co(tmen)_3]^{3+}$ [33] (**1**)	1.994	1.973	1.989
$[Co(NH_2CH_3)_6]^{3+}$ [34]	2.013	1.983	2.008
$[Co(trap)_2]^{3+}$ [35] (**2**)	1.943^{eq}	1.938^{eq}	1.937^{eq}
	1.963^{ax}	1.952^{ax}	1.960^{ax}
[Co(*trans*-diammac)]$^{3+}$ [36,37] (**3**)	1.940^{eq}	1.936^{eq}	1.935^{eq}
	1.947^{ax}	1.943^{ax}	1.947^{ax}
$[Co(dpt)_2]^{3+}$ [38,39] (**4**)	1.977	1.957	1.976
	2.032	1.999	2.030

[a] See Appendix 1 (Supporting Information) for a list of CSD names for the calculation of the average. Numbers in parentheses indicate the structure number in the figure shown in Appendix 1.

Success in reproducing the trend using MM does not, of itself, confirm that the variation observed across the series is entirely steric in origin. However, if the effect was electronic, then it is unlikely that parameters derived to fit the trend would also reproduce bond length changes known to be caused by steric effects. To test this, the new parameters were assessed using a set of Co^{III} hexaamines (complexes **1**−**4**, Table 6) with ligands that encompass a range of steric constraints. It was found that the new parameters derived using the $[Co^{III}N_nO_{6-n}]$ series not only reproduced the hexamine series but did so significantly better than any previously reported parameters, as is illustrated in Table 7. The parameters were also at least as effective as previously reported at reproducing the isomer distribution in the $[Co(dien)_2]^{2+}$ system (Table S12 of the Supporting Information).[2] This indication that the new parameters are valid provides good evidence that the reduction in bond lengths observed across the $[Co^{III}N_nO_{6-n}]$ series is largely steric in origin. However, we cannot rule out an electronic contribution that is linearly dependent on the steric contribution. Similarly, the Co^{III}−O parameters derived were able to reproduce the bond lengths in $[Co^{III}O_6]$ systems (Table S9 of the Supporting Information). However, because of the smaller variation in the Co^{III}−O series, we do not consider the parameters to be as reliably determined as those of Co^{III}−N.

The force constants derived in this way were lower than those previously reported for Co^{III}−N and Co^{III}−O interactions, which were derived from IR spectroscopic data.[31] For instance, the Co^{III}−N force constant is 1.0 mdyn Å^{-1} compared with the previously reported values of 1.5−1.82 mdyn Å^{-1}.[2] The rationale for the lowering of spectroscopically derived force constants for application to MM has been described previously for angle-bend functions.[2,45] Specifically, MM force constants relate to large deviations about a strain-free minimum, whereas vibrational force constants relate to small deviations about a strained minimum. There are also differences in the force fields used. As a result of those differences, force constants for angle-bend functions in MM models are about half those derived from spectroscopic data. It appears from the present study that a similar reduction may be appropriate for the M-ligand force constants.

$[Ni^{II}N_nO_{6-n}]$ Series. The most obvious difference between the $[Ni^{II}N_nO_{6-n}]$ series and the $[Co^{III}N_nO_{6-n}]$ series is the shape of the curves. Those through the Co^{III} series are linear, whereas those through the Ni^{II} series are asymptotic, this asymptotic behavior being most evident in the Ni^{II}−O series. The curves representing the Ni^{II} series have similar shapes, leveling out at the $[Ni^{II}N_2O_4]$ point, indicating that the forces in each series are affecting oxygen and nitrogen donors equally. This is probably indicative of a steric effect because the systematic removal of steric strain from a system must

---

(45) Burkert, U.; Allinger, N. L. *Molecular Mechanics*; American Chemical Society: Washington, D.C., 1982; Vol. 177.
(46) Hendry, P.; Ludi, A. *Adv. Inorg. Chem.* **1990**, *35*, 117−198.
(47) Visser, H. G.; Purcell, W.; Basson, S. S. *Poyhedron* **2001**, *20*, 185−190.

Table 7. Comparison of Molecular Mechanics Results with New Parameters Derived from the [$Ni^{II}N_nO_{6-n}$] Series Compared with Those Reported Previously

compound and refs	exptl	published param[2] ($k_b = 0.6$ mdyn Å^{-1}, $r_0 = 2.090$ Å)	new param ($k_b = 0.3$ mdyn Å^{-1}, $r_0 = 2.042$ Å)
[$Ni(NH_3)_6$]$^{2+}$ [43]	2.131	2.136	2.128
[$Ni(en)_3$]$^{2+}$ [a]	2.131	2.125	2.119
[$Ni(tn)_2$]$^{2+}$ [44,45] (**11**)	2.14	2.149	2.155
[$Ni(dien)_2$]$^{2+}$ [46]	2.135, 2.164, 2.086	2.129, 2.149, 2.088	2.125, 2.159, 2.060
[$Ni(tacn)_2$]$^{2+}$ [47] (**12**)	2.123	2.151	2.156

[a] See Appendix 1 (Supporting Information) for calculation of the average. Numbers in parentheses indicate the structure number in the figure shown in Appendix 1.

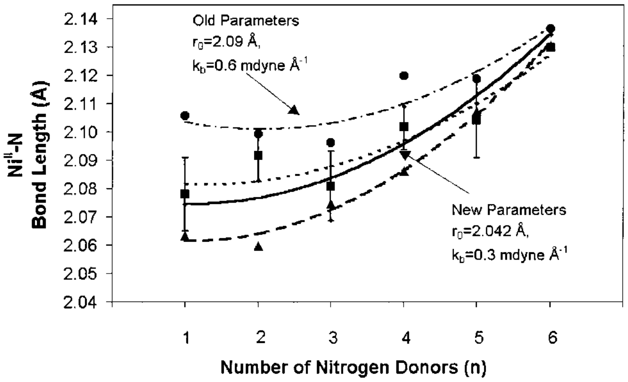

Figure 6. Comparison of molecular mechanics results with statistical analysis for the $Ni^{II}-N$ bond lengths of the [$Ni^{II}N_nO_{6-n}$] series. In each case the lines represent the best fit through the series and the error bars a 95% confidence interval on the mean. Full data analysis for the subset and the molecular mechanics optimized subset is available with the Supporting Information for this paper. (−■−) Full statistical analysis as illustrated in Figure 3. (−▲−) Subset analysis: The average bond lengths of the subset of structures given in Appendix 1 (Supporting Information). (--♦--) Molecular mechanics optimized subset with parameters $k_b = 0.3$ mdyn Å^{-1} and $r_0 = 2.042$ Å. (−•●•−) Molecular mechanics optimized subset with old parameters $k_b = 0.6$ mdyn Å^{-1} and $r_0 = 2.090$ Å.[22,23]

affect both sets of donors simultaneously, but this is not necessarily the case for an electronic effect.

Bond lengths in Ni^{II} complexes are significantly longer than those in Co^{III} complexes (~2.00−2.17 Å as opposed to ~1.89−1.97 Å), and consequently the repulsion between the ligands is less in Ni^{II} than in Co^{III}. At some point the ligand−ligand repulsion must become small relative to the energy required to distort the bond. The point at which this occurs represents a minimum in the potential energy surface defining the metal−ligand interaction, and this is what the asymptote of the curves represents. We are able to reproduce these trends including their asymptotic nature using our force field. In this force field the asymptotes of the Ni^{II} curves represent the $Ni^{II}-O$ and $Ni^{II}-N$ bond lengths in the unsubstituted $Ni^{II}O_6$, $Ni^{II}NO_5$, and $Ni^{II}N_2O_4$ complexes (Figure S7 of the Supporting Information).

The parameters describing the $Ni^{II}-N$ and $Ni^{II}-O$ interactions were refined in a manner analogous to those for the Co^{III} series and reproduced the trends in the $Ni^{II}-N$ and $Ni^{II}-O$ bond lengths across the [$Ni^{II}N_nO_{6-n}$] series as illustrated in $Ni^{II}-N$, Figure 6, and $Ni^{II}-O$, Figure S12 of the Supporting Information. The parameters were able to reproduce both the asymptotic shape and the magnitude of the change observed across the two series. The parameters obtained are as follows: for $Ni^{II}-N$, $k_b = 0.3$ mdyn Å^{-1} and $r_0 = 2.042$ Å; for $Ni^{II}-O$, $k_b = 0.095$ mdyn Å^{-1} and $r_0 = 1.90$ Å. The force constants derived in this manner are, as was the case for Co^{III}, smaller than those reported previously (for $Ni^{II}-N$, 0.6 mdyn Å^{-1})[2], a possible reasoning for which was outlined above.

As for the analogous Co^{III} series, the parameters derived by optimization against the [$Ni^{II}N_nO_{6-n}$] series were tested for their ability to reproduce the bond lengths of each of the [$Ni^{II}N_6$] and [$Ni^{II}O_6$] sets (Tables 7 and S10 (Supporting Information)). The $Ni^{II}-N$ parameters successfully reproduced the bond lengths of the Ni^{II} hexaamine series, but in the case of $Ni^{II}-O$ it was found that parameters that reproduced the "average" of the series did not necessarily reproduce structures on a case-by-case basis. As no parameters had been previously been reported for a $Ni^{II}-O$ bond stretch, attempts were made to optimize the parameters using the [$Ni^{II}O_6$] set independent of those derived from the [$Ni^{II}N_nO_{6-n}$] series. This optimization proved to be significantly more problematic than the optimization of the Co^{III} functions. Reproduction of compressed $Ni^{II}-O$ bond lengths required stronger force constants than elongated $Ni^{II}-O$ bond lengths, but a quadratic function must be symmetrical about r_0. No combination of k_b and r_0 reproduced this effect correctly; however, the r_0 about which a bond could be compressed or elongated appeared constant for $Ni^{II}-O$ at about 2.00 Å. The decrease in k_b as the bond length increased coupled with the fact that the bonds contracted significantly less readily than they could be elongated was indicative of a failure of the quadratic function to adequately describe the $Ni^{II}-O$ interaction. The changes in curvature are more consistent with a Morse function. The potential that produced the magnitude of bond length variation across the [$Ni^{II}N_nO_{6-n}$] series was "left shifted" ($r_0 = 1.90$) and had a very weak force constant ($k = 0.095$). These parameters, while unrealistic in terms of a quadratic function, are consistent with a Morse function over the regions of $Ni^{II}-O$ bond lengths, as illustrated by Figure S13 of the Supporting Information.

Conclusions

We have shown statistically that the M−N and M−O bond lengths in two series of complexes [$Co^{III}N_nO_{6-n}$] and [$Ni^{II}N_nO_{6-n}$] decrease as oxygen donors replace nitrogen donors.

It was demonstrated by the use of MM that the effect can be predicted with a single set of metal−ligand stretch parameters, consistent with it being steric in origin and a result of the larger steric bulk of amine donor groups compared with oxygen donor groups.

The bond-length reduction across the two series provides a means for mapping the energy surface of metal−ligand interactions and hence deriving force constants for the metal−ligand interactions. Previously, bond-stretch functions in MM could only be optimized by using a series of ligands that encompassed a range of outer-sphere geometries. Here we demonstrate that a systematic change to the inner coordination sphere can have the same, if not a larger, effect on bond lengths. The systematic change reveals a distinct asymptote effect in high-spin Ni(II) complexes that gives us further information about the energy surface defining metal−ligand interactions.

Acknowledgment. We would like to acknowledge the use of the Cambridge Crystallographic Database (CSD) for the location of structural data and all who have contributed structures to the database. In addition, we would like to gratefully acknowledge the efforts of Mr T. W. Failes, Ms. R. C. Dolman, and Mr. M. D. Hall for their help in proofreading this manuscript, Dr. P. Turner, Dr. D. E. Hibbs, and Dr. A. R. Battle for assistance in using and referencing the CSD, and the Australian government for R.K.H.'s scholarship.

Supporting Information Available: Text describing those structures used in the "full set" and "subset" analyses recorded using their CSD names and the confidence intervals calculated, tables listing data only recorded in graph form, bond lengths recorded for the subset analysis, and the subsequent MM parametrizations, and figures showing many further plots of both energy surfaces of the MM program and of different aspects of the statistical analysis, a plot comparing the $Ni^{II}-O$ and $Ni^{II}-N$ subset $[NiN_n(H_2O)_{6-n}]$ compared to the $[NiN_nO_{6-n}]$ data set, and statistical and molecular mechanics analysis of structural *trans*-effects. This material is available free of charge via the Internet at http://pubs.acs.org. A copy of the excel spreadsheets containing the crystallographic data is available from the authors.

IC010930Z