and NO_3^- salts studied here, the B/B′ and the B,B′/PtN_4 dihedral angles are relatively large and indicate no intracomplex base/base interaction. In addition, as noted above, there are no intercomplex base-stacking interactions. Instead we find considerable anion interaction with the coordinated bases; see Figure 3–5. For these 1,3,9-TMX complexes, the presence of different counterions in the crystal structure does have a significant influence on the magnitude of the B/B′ dihedral angle—the angle for the PF_6^- salt being nearly 17° larger than that for the NO_3^- salt.

Thus, we conclude for *cis*-bis(N(7)-bound 6-oxopurine)platinum(II) model systems representing the type 1 cross-linking mode that the primary conformational features are determined by competition between intracomplex (base/base, hydrogen bonding) and intercomplex (base/base, base/counterion, hydrogen bonding) interactions. Intracomplex base/base interactions apparently become more important on going from nucleobase complexes to nucleoside complexes to nucleotide complexes. A factor that may be important with regard to the latter complexes is the common occurrence of an O(phosphate)···H–O–H···O(6) hydrogen-bonding scheme.[23] However, a complete understanding of the conformational aspects of type 1 model complexes is yet to be achieved. More work is clearly needed to fully rationalize all factors influencing the conformations of nucleotide, nucleoside, and nucleobase systems.

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Registry No. $[(en)Pt(1,3,9\text{-TMX})_2](NO_3)_2\cdot H_2O$, 79855-87-1; $[(en)Pt(1,3,9\text{-TMX})_2](PF_6)_2$, 79872-71-2; $(en)PtI_2$, 23858-10-8.

Supplementary Material Available: Tables of nonhydrogen anisotropic thermal parameters, parameters for the hydrogen atoms, and calculated and observed structure factor amplitudes for each reported structure (78 pages). Ordering information is given on any current masthead page.

Notes

Contribution from the Chemistry Department,
University of Tasmania, Hobart TAS 7001, Australia

A Simple Method of Estimating the Change in Metal–Ligand Bond Length Accompanying a Rearrangement of the d Electrons in a Transition-Metal Complex

M. A. Hitchman

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It is well-known that a change in the occupancy of the antibonding d orbitals directed toward the ligands in a complex such as often occurs upon light absorption or a high/low-spin interconversion is generally accompanied by a significant alteration in the equilibrium metal–ligand bond distance.[1] A closely related problem concerns the Jahn–Teller distortions associated with an unequal occupancy of the e_g orbitals of an octahedral complex, which are conventionally treated quantitatively by expanding the potential energy of the molecule as a function of the Jahn–Teller active vibrational mode.[2] The purpose of the present note is to point out that an analogous procedure may be used to derive the difference in bond length between two forms of a metal complex having different d-electron configurations, in this case by expanding the potential energy difference between these as a function of the totally symmetric metal–ligand stretching mode.

If it is assumed that the energy separation Δ between the d orbitals involved in the electron change depends inversely on some power n of the bond distance, the change in bond length δr is related to the force constant f of the symmetric stretch by the equation[3]

$$\delta r \simeq \frac{nm\Delta}{fr_0N} \tag{1}$$

which is derived in the Appendix. Here, m is the number of electrons involved in the change, r_0 is the initial bond distance, and N is the number of ligand atoms bonded to the metal. Simple bonding theories, both covalent and electrostatic, and experimental evidence suggest that $n \simeq 5$ at least for the d orbital splitting complex.[4] Using this value, it is of interest to see how the bond length changes estimated with use of eq 1 agree with those deduced for transitions between ground and excited d configurations from electronic spectroscopy and observed by X-ray crystallography for complexes having different spin ground states. It may be noted that a very similar expression to that given in eq 1 may be derived to describe the distorted geometries that result from coupling with Jahn–Teller active modes for metal ions with orbitally degenerated electronic states; this will be the subject of a future publication.

Bond Length Changes Accompanying "d–d" Excitations

It is well established that the width of a "d–d" absorption band depends upon the difference in the equilibrium bond length between the ground and excited state.[1] Recently, quantitative estimates of these differences have been deduced from the spectra of several complexes and the values obtained are shown in Table I together with those estimated with use of eq 1. In each compound the transition is between the $d_{x^2-y^2}$ and d_{xy} orbitals or their equivalents in energy. A single electron is involved in every case except that of $[Cs_2NiCl_4]\cdot CsCl$, for which, because of the effects of interelectron repulsion, $m = 1.75$,[5] and the $^5T_{2g} \leftarrow {}^1A_{1g}$ transition of $Co(NH_3)_6^{3+}$ for which $m = 2$. Agreement between the two sets of values is generally good, the only marked discrepancy occurring for the planar $CuCl_4^{2-}$ ion,[6] for which the value obtained with use of eq 1 is about twice that derived from the

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(1) See, e.g., C. K. Jørgensen, "Absorption Spectra and Chemical Bonding in Complexes", Pergamon Press, 1962, p 98.

(2) D. Reinen and C. Friebel, *Struct. Bonding (Berlin)*, **37**, 1 (1979), and references therein.

(3) An essentially similar expression, applying just to an octahedral complex, is given in ref 7.

(4) D. W. Smith, *Struct. Bonding (Berlin)*, **35**, 105 (1978), and references therein.

(5) T. W. Couch and G. P. Smith, *J. Chem. Phys.*, **53**, 1336 (1970). The number of electrons involved in the relevant transition was obtained from the eigenvectors of the appropriate matrix, and the change in bond length was estimated from the reported relative intensities of the vibrational components of the band due to the $^3A_2 \leftarrow {}^3T_1(F)$ transition with use of the tables in: J. R. Henderson, R. A. Willett, M. Muramoto, and D. C. Richardson, "Douglas Reports SM-45807, Jan. 1964".

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Table I. Change in Metal–Ligand Bond Distance δr Accompanying d–d Excitations Estimated from Electronic Spectra and Calculated with Use of Eq 1[s]

compd	stereochem	Δ, cm^{-1}	ν_{a_1}, cm^{-1} ground	ν_{a_1}, cm^{-1} excited	ground-state force const,[f] mdyn/Å	r_0, Å	δr, Å spectra	δr, Å calcd
$Co(NH_3)_6(ClO_4)_2Cl\cdot 2KCl$	octahedral	24 000[a]	498[b]	480[a,c] 435[a,d]	2.49	1.97[b]	0.07[a,c] 0.12[a,d]	0.08 0.16
Cs_2PtF_6	octahedral	31 500[e]	590[e]	500[e]	3.90	1.91[g]	0.08[e]	0.07
$[Cr(NH_3)_6](ClO_4)_2Cl\cdot 2KCl$	octahedral	22 320[h]	462[h]	403[h]	2.14	2.06[h]	0.07[h]	0.08
K_2PtCl_4	planar	25 961[i]	329[d]	290[d]	2.26	2.33[j]	0.08[i] 0.10[d]	0.12
K_2PtBr_4	planar	24 217[k]	205[d]	170[d]	1.98	2.46[l]	0.10[d]	0.12
K_2PdCl_4	planar	21 491[m]	310[m]	271[m]	2.01	2.29[m]	0.11[m]	0.12
K_2PdBr_4	planar	20 051[k]	190[k]	166[k]	1.70	2.46[n]	0.10[k]	0.12
$(C_6H_5C_2H_4NH_2CH_3)_2CuCl_4$	planar	12 500[o]	276[o]	272[o]	1.59	2.26[p]	0.05[o]	0.09
$[Cs_2NiCl_4]\cdot CsCl$	tetrahedral	3 045[q]	292[q]	285[q]	1.78	2.245[r]	0.03[q]	0.03

[a] R. B. Wilson and E. I. Solomon, *J. Am. Chem. Soc.*, **102**, 4085 (1980). [b] Data from ref 8. [c] Value for the single-electron $^1T_{1g} \leftarrow {}^1A_{1g}$ transition. [d] Value for the double-electron $^5T_{2g} \leftarrow {}^1A_{1g}$ transition. [e] H. H. Patterson, W. J. DeBerry, J. E. Byrne, M. T. Hsu, and J. A. LoMenzo, *Inorg. Chem.*, 16, 1698 (1977). [f] Calculated from ν_{a_1} (ground state). [g] D. P. Mellor and N. C. Stephenson, *Aust. J. Sci. Res., Ser. A*, 4, 406 (1951). [h] Reference 6. [i] H. H. Patterson, J. J. Godfrey, and S. M. Khan, *Inorg. Chem.*, 11, 2872 (1972). [j] R. G. Dickinson, *J. Am. Chem. Soc.*, 44, 2404 (1922). [k] T. G. Harrison, H. H. Patterson, and M. T. Hsu, *Inorg. Chem.*, 15, 3018 (1976). [l] N. C. Stephenson, *Acta Crystallogr.*, 17, 587 (1964). [m] T. G. Harrison, H. H. Patterson, and J. J. Godfrey, *Inorg. Chem.*, 15, 1291 (1976). [n] Von K. Broderson, G. Thiele, and H. Gaedke, *Z. Anorg. Allg. Chem.*, 348, 162 (1966). [o] Reference 5. [p] R. L. Harlow, W. J. Wells III, G. W. Watt, and S. H. Simonsen, *Inorg. Chem.*, 13, 2106 (1974). [q] Reference 4. [r] G. D. Stucky, J. B. Folkers, and T. J. Kistenmacher, *Acta Crystallogr.*, 23, 1064 (1967). [s] In the references given under footnotes *e, i, k, m,* and *o* the values of Q are incorrectly interpreted as representing values of δr.

electronic spectrum. The a_{1g} stretching mode also changes by an abnormally small amount in this case (see Table I), and because of this it was suggested[6] that the complex may have a distorted tetrahedral geometry in the excited state; possibly this modifies the increase in the Cu–Cl bond distance accompanying the electron excitation. In agreement with the model, the bond length change accompanying the $^5T_{2g} \leftarrow {}^1A_{1g}$ double-electron excitation in the $Co(NH_3)_6^{3+}$ ion is about twice that observed for the $^1T_{1g} \leftarrow {}^1A_{1g}$ single-electron excitation. The bond length changes in the planar ions PdX_4^{2-} and PtX_4^{2-}, X = Cl or Br, are all quite similar, being ~50% greater than those in the octahedral complexes. This is due largely to the smaller number of ligands bound to the metal (N in eq 1). The most severe test of the model comes in its application to the change in bond distance expected to accompany the $e \rightarrow t_2$ transition of a tetrahedral complex. Here, the force constant and bond lengths are comparable to those in the planar ions, but the very low Δ value means that the bond distance is expected to increase by only a small amount. Analysis of the vibrational fine structure reported for the $^3T_1(F) \rightarrow {}^3A_2$ transition of Ni^{2+} doped into $[Cs_2ZnCl_4]\cdot CsCl$[5] suggests a bond length change in good agreement with the theoretical value, implying that the model is satisfactory over a wide range of ligand types, metal oxidation states, and complex stereochemistries.

If it is realistic, the model should predict the same change irrespective of which configuration is used as a starting point. In the case of the $Cr(NH_3)_6^{3+}$ ion this may be tested, as the Δ value in the excited state is known to be ~17 600 cm^{-1}.[7] Substitution of this in eq 1, together with the force constant and bond length of the excited state, yields a predicted change in Cr–N distance on going from the $(t_2)^2(e)$ to the $(t_2)^3$ configuration identical with that estimated for the reverse process. The model is thus self-consistent in this respect. It is perhaps surprising that such a simple model works so well, using as it does a simple harmonic potential for the vibrational function and an expansion of the electronic potential carried out only to first order. One reason may be the fact that an anharmonicity correction to the vibrational potential and the second-order term of the electronic potential should act in an opposite sense and could well cancel one another.

Bond Length Variations Accompanying High/Low-Spin Interconversions

Specific data on vibrational force constants are unfortunately not yet available for complexes that exist in two different spin states. However, the substitution in eq 1 of the a_{1g} force constant estimated for the $Fe(NH_3)_6^{2+}$ ion (1.2 mdyn/Å)[8] together with the average bond length r_0 = 2.18 Å observed for several high-spin iron(II) amine complexes[9,10] and a value of Δ = 12 500 cm^{-1} yields an estimate of $\delta r \simeq 0.16$ Å for the shortening in each Fe–N bond on going to the analogous low-spin complex. In the case of a cobalt(II) complex, the contraction should be about half this, as only a single electron is involved in the spin change (note, however, that this latter situation is expected to be complicated by the presence of a Jahn–Teller distortion in the low-spin form). These values are in excellent agreement with the differences in ionic radii for high- and low-spin Fe^{2+} and Co^{2+} estimated by Shannon and Prewitt (0.16 and 0.085 Å, respectively).[11] Recent crystal structure determinations suggest that the Fe(II) bond distance is consistently 0.17–0.19 Å shorter in a low-spin complex compared with that of the analogous high-spin compound.[9,10] Comparable experimental data for cobalt(II) are scarce. The average metal–ligand bond distance in low-spin Co(salen)·py is 0.08 Å less than that in high-spin Co(3-MeOsalen)·H_2O,[12] while the average bond length in the low-spin $Co(NO_2)_6^{4-}$ ion is ~0.1 Å less than that in the analogous nickel(II) species[2] (which has an e_g electron configuration identical with that of a high-spin Co(II) complex). All in all, therefore, the model is in reasonable agreement with such experimental observations as are available. It has been suggested[9] that high/low-spin interconversions are accompanied by significantly smaller bond

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(7) R. B. Wilson and E. Solomon, *Inorg. Chem.*, **17**, 1729 (1978).

(8) Estimated from data quoted in K. H. Schmidt and A. Müller, *Coord. Chem. Rev.*, **19**, 41 (1976). Note the force constant is that of the a_{1g} totally symmetric stretching vibration, not that normally quoted as the $M–NH_3$ force constant.

(9) A. M. Greenway and E. Sinn, *J. Am. Chem. Soc.*, **100**, 8080 (1978).

(10) B. A. Katz and C. E. Strouse, *J. Am. Chem. Soc.*, **101**, 6214 (1979); M. Mikrami, M. Konno and Y. Saito, *Chem. Phys. Lett.*, **63**, 566 (1979).

(11) R. D. Shannon and C. T. Prewitt, *Acta Crystallogr., Sect. B*, **B25**, 925 (1969).

(12) M. Calligaris, D. Minichelli, G. Nardin, and L. Randaccio, *J. Chem. Soc. A*, 2411 (1970); M. Calligaris, G. Nardin and L. Randaccio, *J. Chem. Soc., Dalton Trans.*, 1903 (1974).

length changes in Fe(III) complexes than is the case for similar Fe(II) compounds. Unfortunately, reasonable estimates of force constants and Δ values are as yet unavailable for complexes of the former ion. However, the present model suggests that for the same value of m the most important factor influencing bond length changes would be the ratio Δ/f, so that the experimental observations could be explained if f increases by a significantly greater amount than Δ, on going from the iron(II) to the iron(III) species. It is noteworthy that smaller structural changes are in general predicted for compounds involving ligands that form strong bonds but produce a relatively small splitting of the d orbitals such as might be the case for some sulfur-donor ligands. Substitution of the data appropriate to the $Co(NH_3)_6^{3+}$ ion into eq 1 ($m = 2$, $\Delta = 21000$ cm^{-1},[1] $f = 2.49$ mdyn/Å,[8] $r_0 = 1.97$ Å[13]) yields a value or $r_0 \simeq 2.11$ Å for the bond length predicted for the high-spin form of this ion. This is very similar to the value of 2.114 Å observed[14] for the high-spin $Co(NH_3)_6^{2+}$ ion, which is in agreement with the suggestion[15] that for complexes involving non-π-bonding ligands a change in the charge on the metal has little effect on the metal–ligand bond distance.

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Appendix

Consider two electron configurations of a metal complex differing in the distribution of m electrons between d orbitals separated in energy by an amount Δ. The energy of the second configuration relative to the first at bond length r_0 is given by

$$U = m\Delta + S$$

where S represents any contribution due to interelectron repulsion terms such as the so-called spin-pairing energy. Consider the effect of an expansion Q in the totally symmetric stretching mode of force constant f.[16] With the assumption that Δ is inversely proportional to the nth power of the bond length

$$U = \frac{f}{2}Q^2 + m\Delta\left[\frac{r_0 + CQ}{r_0}\right]^{-n} + S$$

where C is a normalization constant. For small values of CQ/r_0

$$U \simeq \frac{f}{2}Q^2 + m\Delta\left[1 - \frac{nCQ}{r_0}\right] + S$$

The displacement Q corresponding to a mininum energy of the second electron configuration is obtained by setting $\mathrm{d}U/\mathrm{d}Q = 0$, and as to a first approximation S is independent of Q, this gives

$$Q = \frac{mnC\Delta}{fr_0}$$

The change in each bond length is given by $\delta r = CQ$, where for the totally symmetric mode $C = 1/N^{1/2}$, N being the number of ligand atoms. It therefore follows that

$$\delta r = \frac{mn\Delta}{fr_0N}$$

Note that for both Δ and f the appropriate values are those of the initial state of bond length r_0.

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(13) This represents an average Co(III)–NH_3 bond distance; see ref 8, p 87.

(14) T. Barnet, B. M. Craven, H. C. Freeman, N. E. Kine, and J. A. Ibers, *Chem. Commun.*, 307 (1966).

(15) N. J. Hair and J. K. Beattie, *Inorg. Chem.*, **16**, 245 (1977).

(16) The bond length change is conveniently calculated in Å with use of the relationship 1 mdyn/Å = 0.5035 × 10^5 cm^{-1} Å^{-2}.

Contribution from the Chemistry Department,
University of Tasmania, Hobart, Tasmania 7001, Australia

Polarized Crystal Spectrum of $Ni(NH_3)_4(NO_2)_2$: Non-"d-d" Assignment of the Band Centered at 20000 cm^{-1}

Michael A. Hitchman* and Graham L. Rowbottom

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As part of a general investigation of the electronic and structural properties of transition-metal nitrite complexes, we have measured[1] the electronic spectrum of the (001) crystal face of the trans nitro complex $Ni(NH_3)_4(NO_2)_2$ at 10 K (see Figure 1); the room-temperature spectrum has been reported previously by Hare and Ballhausen.[2] The crystal structure of the compound has been described by Porai-Koshits[3] and, more recently, by Figgis et al.[4] The spectrum is conveniently discussed in terms of three regions, considered in order of decreasing energy (see Table I).

Region I (26000–28000 cm^{-1}). The b spectrum consists of three progressional band systems, each of interval 620 ± 25 cm^{-1}. Only two peaks can be resolved in the more intense a spectrum, with the lower energy one almost coinciding in position with that in b polarization. In this region the spectrum is quite similar to that reported[5] for $NaNO_2$, which shows a series of progressions of interval 632 ± 4 cm^{-1} assigned to the nitrite wagging mode δ_{NO_2} (ground-state energy 829 cm^{-1}) built upon an origin at 25977 cm^{-1} and involving the excitation of single quanta of various lattice modes. In the case of $NaNO_2$ there has been general agreement that the overall band is due to the $^1B_2 \leftarrow {}^1A_1$ nitrite n → π^* transition. However, the nature of the nonbonding orbital has been the subject of debate. Early work[5] suggested that this was localized largely on the nitrogen atom, and this view was supported by Fee et al.[6] who observed an analogous band in several chromium(III) nitrito complexes. Recent calculations[7] and the behavior of the n → π^* band in various hydroxylic solvents[8] both suggest that the nonbonding orbital is localized largely on the oxygen atoms. If, as seems likely, the band in $Ni(NH_3)_4(NO_2)_2$ is due to the same transition as that in $NaNO_2$, then the latter propositon seems more plausible, as in the nickel complex the nitrogen lone-pair electrons are involved in bonding to the metal. This interpretation then assigns the peaks in region I of the spectrum of $Ni(NH_3)_4(NO_2)_2$ to an n(O) → π^* internal nitrite transition involving progressions in the nitrite wagging mode δ_{NO_2}, built upon an electronic origin at 26260 ± 5 cm^{-1} and with the additional excitation of one quantum of vibrational modes of energy ~260 cm^{-1} (b system 3), 440 cm^{-1} (b system 2), and ~310 cm^{-1} (a). The vibrations of energy 260 and 310 cm^{-1} are likely to be metal–nitrite stretches or bends, while that of energy 440 cm^{-1} must be due to the metal–nitrite wagging mode ρ_w, which characteristically occurs at 450 cm^{-1} in nickel(II) nitro complexes.[9]

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(1) The compound was prepared by the method in W. G. Palmer, "Experimental Inorganic Chemistry", Cambridge University Press, New York, 1954, p 559. Physical measurements were made with use of a Cary 17 spectrophotometer and a Cryodine Model 21 cryostat.

(2) C. R. Hare and C. J. Ballhausen, *J. Chem. Phys.*, **40**, 792 (1964).

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(8) S. J. Strickler and M. Kasha, *J. Am. Chem. Soc.*, **85**, 2899 (1963).

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