$(CN)_4^{2-}$ complex may be estimated from a measured ^{14}N line width, $\nu_{1/2}$, of 750 ± 100 Hz at 300 ± 2 K. Measurements were carried out at 14.4 MHz on a Bruker WH-200 spectrometer. Since ^{14}N relaxation is completely dominated by quadrupole relaxation,[2–4,9] τ_{eff} is estimated to be 13.2 ps by using eq 2 where e^2qQ/h, the ^{14}N quadrupole coupling constant, is taken to be 3.467 MHz, the value measured for $K_2Pt(CN)_4$.[10] Because of uncertainties in $\nu_{1/2}$ and e^2qQ/h, the error in τ_{eff} is estimated to be as large as 20%. Despite this, it is clear that the ^{14}N–^{13}C dipole–dipole relaxation also makes a significant contribution to the spin–lattice relaxation of the cyano carbon. Taking the carbon–nitrogen bond length, r_{CN}, as 1.13 Å[11] in eq 3[4] leads to $T_1(^{14}N-^{13}C)^{DD} = 316$ s. Thus this contribution together with the CSA mechanism accounts for about 60% or more of the observed relaxation in $Ni(CN)_4^{2-}$. Both of these mechanisms give rise to longer T_1's with increasing temperature as observed by Pesek and Mason.[1] Other significant contributions to T_1 may result from paramagnetic impurities or intermolecular dipole–dipole relaxation with solvent spins (deuterium and possibly some proton impurities such as HOD).

$$\tau_{\text{eff}} = \frac{2}{3\pi}\,\frac{\nu_{1/2}}{(e^2qQ/h)^2} \qquad (2)$$

$$\frac{1}{T_1(^{14}\text{N}-^{13}\text{C})^{\text{DD}}} = \frac{8}{3}\,\frac{\gamma_{\text{N}}^2\gamma_{\text{C}}^2\hbar^2}{r_{\text{CN}}^6}\,\tau_{\text{eff}} \qquad (3)$$

Finally we wish to point out that scalar relaxation to ^{14}N is unimportant for spin–lattice relaxation of the cyano carbons in $Ni(CN)_4^{2-}$ and any other of the complexes investigated by Pesek and Mason.[1] The contribution of this mechanism is given by eq 4 where $A = 2\pi(^1J(^{14}N,^{13}C))$, $S = 1$, and $\tau_S = T_2(^{14}N)$.[2–4] Using ^{15}N-labeled cyanide, we have prepared ^{15}N-enriched (95%) $K_2Ni(CN)_4$ and measured $^1J(^{15}N,^{13}C) = 9.3 \pm 0.2$ Hz; thus $^1J(^{14}N,^{13}C) = 6.6 \pm 0.2$ Hz and $A = 41.6 \pm 1$ rad s^{-1}. Substitution of ω_C and ω_N at 2.35 T and the measured value of τ_S gives $T_1(SC) = 2.3 \times 10^9$. Similarly substitution into standard expressions for the scalar contribution to T_2 gives 2 s. Therefore, the ratio of $T_1(SC)/((T_2(SC)) \simeq 10^9$, contrary to the value estimated in ref 1.

$$\frac{1}{T_1(\text{SC})} = \frac{2}{3}A^2S(S+1)\frac{\tau_{\text{S}}}{1+(\omega_{\text{C}}-\omega_{\text{N}})^2\tau_{\text{S}}^2} \qquad (4)$$

Since the rotational correlation times of most of the cyano complexes investigated by Pesek and Mason[1] are of the same order of magnitude[9,12] as those measured for $K_2Ni(CN)_4$, the chemical shielding anisotropy and ^{13}C–^{14}N dipole–dipole mechanisms must also make substantial contributions to T_1 in these complexes.[13] Although scalar coupling to ^{14}N is not important for ^{13}C spin–lattice relaxation, it will make a significant contribution to ^{13}C spin–spin relaxation in these complexes.

Acknowledgment. We wish to thank Mr. G. Bigam and Dr. T. Nakashima for the ^{14}N measurements and their assistance in using the Bruker WH-400 (Department of Chemistry, University of Alberta) and Dr. G. Kotowycz and Dr. T. Nakashima for making high-field spectrometer time available for this project. Financial support from the Natural Sciences and Engineering Research Council of Canada is gratefully acknowledged.

Registry No. $K_2Ni(CN)_4$, 14220-17-8.

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(8) (a) Using $T_1(CSA) = 12.9$ s and $\tau_{\text{eff}} = 13.2$ ps in the expression $T_1(CSA)^{-1} = {}^2/_{15}(\gamma_C B_0)^2(\Delta\sigma)^2\tau_{\text{eff}}$, which assumes axial symmetry, we estimate $\Delta\sigma = 330 \pm 50$ ppm for the cyano carbon in $Ni(CN)_4^{2-}$. This is in good agreement with values of $\Delta\sigma(^{13}C)$ obtained in organic nitriles[8b,c] and for the cyano ligand in $K_2Pt(CN)_4Br_{0.3}\cdot 3H_2O$.[8d] Note that the shielding tensor for the cyano ligand is only approximately axially symmetric.[8d] (b) Vold, R. R.; Vold, R. L.; Szeverenyi, N. M. *J. Chem. Phys.* **1979**, *70*, 5213. (c) Wehrli, F. W. *J. Magn. Reson.* **1978**, *32*, 451. (d) Stoll, M. E.; Vaughan, R. W.; Saillant, R. B.; Cole, T. *J. Chem. Phys.* **1974**, *61*, 2896.

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(13) From ^{13}C T_1 measurements of $K_2Pt(CN)_4$ at 100.6 and 20 MHz, we estimate $T_1(CSA) \le 12.4$ s for the cyano carbon at 9.39 T. Measurements were carried out in deuterium oxide solutions at 300 ± 2 K.

The Sense of Jahn–Teller Distortions in Octahedral Copper(II) and Other Transition-Metal Complexes

Sir:

The large, predominantly tetragonal, distortions observed in octahedral copper(II) complexes are frequently cited to illustrate the Jahn–Teller effect in transition-metal complexes. The driving force for these distortions follows qualitatively from the unequal electron occupancy of the d orbitals comprising the formal e_g set of the undistorted precursor. Yet as Orgel observed[1] many years ago, "It is a curious and characteristic situation that one is able to predict with certainty that the octahedral environment is unstable and yet one is not able to predict with confidence the nature of the most stable distorted configuration". The distorting force undoubtedly involves several different detailed mechanisms, but we consider here one particular contribution which offers a ready explanation of the empirical observation that almost all octahedral copper(II) (and chromium(II)) complexes suffer tetragonal *elongations*.

Considerable evidence is accumulating in the literature for configurational mixing of higher lying s orbitals into the ligand field d orbital basis. In the D_{4h} symmetry of planar complexes, for example, 4s and $3d_{z^2}$ functions both transform as a_{1g} and can mix, studies of planar iron(II),[2] cobalt(II),[3,4] nickel(II),[5] and copper(II)[6] systems having demonstrated that such mixing is extensive enough to depress the energy of the $3d_{z^2}$ orbital by up to 6000 cm^{-1} relative to its energy as predicted by various ligand field models based solely upon the 3d orbital basis. Smith[6] has argued that such an effect is important even in several nonplanar copper(II) species. Evidence for d–s mixing relies not only upon the eigenvalues of the d_{z^2} orbital in various systems but also upon the eigenvector as revealed by ESR studies in which the magnitudes of the scalar hyperfine coupling constants in some planar cobalt(II) systems,[3,4,7] for example, are rationalized in terms of a negative contribution from

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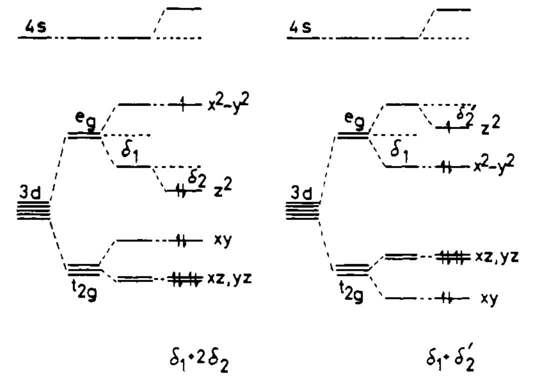

Figure 1. Tetragonal distortions from octahedral precursors in d^9. Stabilization energies with respect to O_h symmetry are shown on the left for elongated octahedra and on the right for compressed octahedra.

the more expanded (higher lying) 4s function.

The qualitative effect of d–s configurational mixing in tetragonally distorted octahedral copper(II) systems is illustrated in Figure 1. Only the d$_{z^2}$ orbital suffers admixture of the 4s function, being depressed energetically by, e.g., δ_2 in the elongated octahedron or by δ_2' under compression. Unless δ_2' is twice the magnitude of δ_2, the elongated distortion is clearly favored. We may expect that the extent of d–s mixing increases as the distortion increases from octahedral to planar D_{4h}, certainly in a more than linear fashion with respect to the extent of the distortion. In effect, the magnitude of the distortion and the degree of d–s mixing reinforce each other, a limit being reached when the net driving forces for distortion are balanced by the loss of bonding energy within the "core" orbitals. We envisage that the contribution to the distortion force from d–s mixing achieves importance only in conjunction with contributions from other mechanisms. This is important, for otherwise the d–s mixing process might lead to a significant tendency of octahedral d^8 or d^{10} complexes to distort, for example. On the other hand, when other mechanisms are important, the d–s configurational mixing confirms the distortion, so to speak, and favors tetragonal elongation rather than compression when the d$_{z^2}$ and d$_{x^2-y^2}$ orbitals are unequally occupied.

Even when these two orbitals are equally occupied, the d–s mixing process should provide a driving force for distortion, though without any preference for its sense, but again to a significant extent only in the presence of other distorting forces. The planar coordination of low-spin nickel(II) or cobalt(II) complexes will gain additional stability from this mechanism. Similarly the large magnitudes of tetragonal distortions in tetrahedrally coordinated copper(II) complexes must derive in part from the d–s configurational mixing, though here, the preference for tetragonal compression presumably derives from the unequal occupancies of the t$_2$ orbitals as shown in Figure 2.

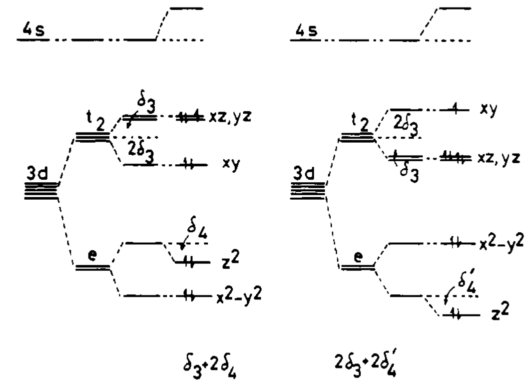

Figure 2. Tetragonal distortions from tetrahedral precursors in d^9 Stabilization energies with respect to T_d symmetry are shown on the left for elongated tetrahedra and on the right for compressed tetrahedra.

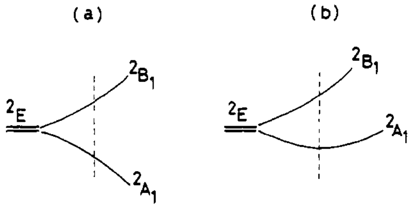

Figure 3. Two possible behaviors of components of ^{2}E. The Jahn–Teller "effect" operates everywhere in part a but only to the left of the broken line in part b.

The Jahn–Teller effect ultimately depends upon the unequal electron occupancy of formally degenerate orbitals. Burdett[8] has identified a stereochemical distortion mechanism which depends only upon the incomplete occupancy of one or more antibonding d orbitals. He argues that the total occupancy (or fullness) of the second highest orbital in d^9 and low-spin d^8 complexes implies, to a first approximation, no net bonding involving that orbital, hence rationalizing the planarity of low-spin nickel(II) species and the long, weak axial bonds in tetragonally elongated copper(II) complexes. There is an inherent symmetry in Burdett's argument, however, in that a reversal of the energies of d$_{z^2}$ and d$_{x^2-y^2}$ as the two highest antibonding orbitals would lead to similar rationalizations of axially compressed geometries in these systems. The d–s configurational mixing mechanism proposed here appears to offer the most direct interpretation of the observed sense of distortion in d^9 (and high-spin d^4) octahedra though we might imagine that it achieves an equal or even dominant role through the driving force identified by Burdett.

Burdett points out that the mechanism he proposed will operate even when the precursor geometry is already of low enough symmetry not to leave an orbitally degenerate ground term, for example, in "octahedral" copper(II) systems with dissimilar or bridging ligands. He goes on to suggest, however, that in these circumstances one should not talk of the Jahn–Teller effect as the Jahn–Teller theorem applies only to orbitally degenerate terms. We would argue that such a view is pedantic, however, for all mechanisms favoring distortion must be supposed to operate at *and around* that point in structure configurational space defining exact orbital degeneracy. In Figure 3 are illustrated just two possible energy diagrams for the ^{2}A$_1$ and ^{2}B$_1$ levels in "octahedral" d^9 systems. The group-theoretical, Jahn–Teller *theorem*[9,10] requires the linear, "barycenter" behavior of these levels close to the degenerate ^{2}E precursor. However, the mechanism of this splitting need not cease once the degeneracy is raised nor even if the splitting is large enough to preclude significant population of the higher component. If we suppose the vertical broken lines in Figure 3 represent precursor geometries as imposed by constraints of ligand dissimilarirty, chelation, bridging, etc., then, in the case shown in Figure 3a, the driving forces for distortion continue to operate, and we expect the molecule to distort even more. In the case of Figure 3b, various second-order effects have contrived to balance the first-order ones such that no further distortion is favored. In the absence

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of exact orbital degeneracy, the Jahn–Teller theorem fails to *require* a first-order, "barycenter" behavior of the levels and so in this sense is irrelevent to the problem. However, the various mechanisms leading to distortion, dependent in many cases upon the unequal electron occupancy of the d orbital pair, continue to be relevent, and we might reasonably continue to refer to the whole phenomenon as the (static) Jahn–Teller *effect*.

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Additions and Corrections

1979, Volume 18

Goji Kodama* and Mitsuaki Kameda: Bis(trimethylphosphine) Adduct of Tetraborane(8).

Page 3302. In the right column, fourth line of the second paragraph, "41.7 ppm" should read "−41.7 ppm".

Page 3306. In the third line of footnote 24, "a single doublet signal" should read "a single broad signal".—Goji Kodama