of $(CO)_4CoSiMe_2$–X–$SiMe_2Co(CO)_4$ (X = O, CH_2) decompose at −78 °C, purified samples of η^6-[1,4-$(CO)_4CoSiMe_2$–C_6H_4–$SiMe_2Co(CO)_4$]$Cr(CO)_3$ could be stored for several weeks under a nitrogen atmosphere at room temperature in the dark without any apparent decomposition. Likewise, solutions of the compound in methylene chloride were stable for several hours in a nitrogen atmosphere, although when the solutions were exposed to air, decomposition was accelerated appreciably.

In order to see if the coordination of the $Cr(CO)_3$ entity had a part in the improved stability, we undertook the preparation of the uncomplexed analogue 1,4-$(CO)_4CoSiMe_2$–C_6H_4–$SiMe_2Co(CO)_4$. This compound was obtained by the reaction of 1,4-$HSiMe_2$–C_6H_4–$SiMe_2H$ with $Co_2(CO)_8$. The infrared and proton NMR spectra of the compound were very similar to those of the analogous $Cr(CO)_3$ complex described above except that the two A_1 and E $Cr(CO)_3$ absorptions were absent in the infrared spectrum and the position of the C_6H_4 protons in the NMR spectrum was at a lower field position (δ 7.21) than in the spectrum of the complex. The compound was reasonably stable thermally but not nearly as stable as the analogous $Cr(CO)_3$ complex. It slowly acquired a violet color when stored as a solid in a nitrogen atmosphere at room temperature overnight. After 2 weeks under these conditions, the material was a gray-brown powder. The pure compound dissolves readily in cyclohexane, and there was no obvious color change when fresh solution samples were taken for infrared analysis. However, after several hours under these conditions, the solution acquired a purple color. New absorptions appeared in the spectrum which corresponded to the major bands found in $Co_2(CO)_8$. The solution darkened further when the sample was held in solution at room temperature for longer time periods. Samples of the pure compound and solutions of the material rapidly acquired a dark brown color when exposed to air.

We conclude from these observations that the thermal stability of bis((tetracarbonylcobaltio)dimethylsilyl) derivatives is influenced by the nature of the bridging group. The derivatives containing the bridging aromatic groups (para positions are more stable than those that contain bridging oxygen, nitrogen (NH), or alkyl groupings. The chromium tricarbonyl complex of the bridged aromatic system is considerably more stable than the analogous uncomplexed derivative. All of the systems have a marked tendency to decompose in solution. We have not been able to establish the exact decomposition pathways of the decompositions observed, although $Co_2(CO)_8$ appears to be one of the initial decomposition products in solution.

Registry No. η^6-[1,4-$(HSiMe_2)_2C_6H_4$]$Cr(CO)_3$, 75830-40-9; η^6-[1,4-$(CO)_4CoSiMe_2$–C_6H_4–$SiMe_2Co(CO)_4$]$Cr(CO)_3$, 75830-41-0; 1,4-$(CO)_4CoSiMe_2$–C_6H_4–$SiMe_2Co(CO)_4$, 75830-42-1; $Cr(CO)_6$, 13007-92-6; $Co_2(CO)_8$, 10210-68-1.

Correspondence

Interpretation of ^{13}C NMR Relaxation Times in $K_2Ni(CN)_4$ and Other Diamagnetic Cyano Complexes

Sir:

Recently carbon-13 NMR relaxation times were reported for several diamagnetic cyano complexes.[1] Except for $Fe(CN)_6^{4-}$, which was thought to be contaminated by paramagnetic impurities, the carbon-13 spin–lattice relaxation times, T_1's, for the cyano carbons of these complexes exceeded 30 s. Carbon-13 spin–spin relaxation times, T_2's, were however much shorter, ranging between 0.11 and 0.64 s at 303 K. All reported measurements were carried out for potassium salts of the complexes in aqueous (D_2O) solution. The observed ratios of T_1/T_2 (10^2–10^3) and the generally observed increase in T_1 with increasing temperature led Pesek and Mason[1] to conclude that the mechanism for ^{13}C relaxation (T_1 and T_2) in these complexes is consistent with scalar coupling of the second kind to nitrogen-14.[2–4] In this correspondence we present evidence which indicates that the chemical shielding anisotropy (CSA) and ^{14}N–^{13}C dipole–dipole mechanisms are important for spin–lattice relaxation in $Ni(CN)_4^{2-}$ at the applied field used in ref 1 (2.35 T) and show that although scalar coupling of the second kind is important for spin–spin relaxation, its contribution is negligible for spin–lattice relaxation.

Carbon-13-enriched (50%) potassium tetracyanonickelate(II) was prepared from $K^{13}CN$ and $Ni(CN)_2$ as previously described.[5] A 0.5 M solution of $K_2Ni(CN)_4$ in deuterium oxide was degassed under vacuum by the freeze–pump–thaw technique. Spin–lattice relaxation times were measured at 300 ± 2 K with use of the inversion recovery sequence at 20 MHz (1.87 T), on a Varian CFT-20 spectrometer and at 100.6 MHz with use of Bruker WH-400 (9.39 T) spectrometer. The ^{13}C T_1's calculated with the use of a nonlinear three-parameter least-squares fitting procedure[6] were 97 ± 9 s at 20 MHz and 11.4 ± 0.8 s at 100.6 MHz. The $\pi/2$ pulses at these frequencies were 16 and 20 μs, respectively.

Since chemical shielding anisotropy is the only mechanism for spin–lattice relaxation which can lead to shorter T_1's at higher fields under extreme narrowing conditions, the above data imply that the CSA mechanism completely dominates at 100.6 MHz. Assuming that the rates of relaxation are additive (eq 1) and that T_1(other) ≥ 97 s at 100.6 MHz leads to $T_1(\mathrm{CSA}) \leq 12.9$ s. Since $1/(T_1(\mathrm{CSA}))$ depends on the

$$\frac{1}{T_1(\mathrm{obsd})} = \frac{1}{T_1(\mathrm{CSA})} + \frac{1}{T_1(\mathrm{other})} \qquad (1)$$

square of the applied field, T_1(CSA) is less than or equal to 325 s at 20 MHz and 208 s at 25 MHz. Although the errors in these estimates of T_1(CSA) are at least 10%, it is apparent that the chemical shielding anisotropy mechanism plays a significant role in ^{13}C relaxation at 25 MHz (2.35 T).[8]

The effective rotational correlation time, τ_{eff}, for the Ni-

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$(CN)_4^{2-}$ 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 con-

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

stant, 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

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

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).

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 $\tau_S =$

$$\frac{1}{T_1(SC)} = \frac{2}{3}A^2S(S+1)\frac{\tau_S}{1 + (\omega_C - \omega_N)^2\tau_S^2} \qquad (4)$$

$T_2(^{14}N)$.[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.

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 $\tau_{\mathrm{eff}} = 13.2$ ps in the expression $T_1(CSA)^{-1} = {}^2/_{15}(\gamma_C B_0)^2(\Delta\sigma)^2\tau_{\mathrm{eff}}$, 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 $T_1(CSA) \leq 12.4$ 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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