According to their crystal structures,[3,19] both molecules have D_{2h} symmetry, implying four equivalent nitrogens. Intermolecular interactions alone cannot account for a chemical shift as large as 1.0 eV.

The multiplet splitting hypothesis requires the existence of a biradical that EPR measurements[2] do not support. Moreover the observed 1:3 ratio in the XPS N 1s line does not agree with the calculated 1:2 ratio in the case of a biradical.

Several works on $(SN)_x$ have reported plasmon excitations during photoemission.[20,21] Such collective oscillations need a conductive medium and may not be involved in the cases of $(NSN)_2$ and $(NSeN)_2$.

Sample degradation is unlikely. The chemical inertness of these compounds is well established.[2] Surface oxygen contamination remains negligible, and regular control of core-levels lines does not show any alteration under irradiation. Measurements performed under the same conditions at 4 months interval are perfectly reproducible.

The last possibility we have investigated was to attribute this component to a shake-up transition. In organic compounds, such as the lowest acenes, these transitions present a large amplitude (2–10 eV) and give rise to satellites of weak intensity, typically less than 10% of the main peak.[22] As the two highest occupied π levels ($4b_{1u}$ and $2b_{2g}$) have already been involved in the explanation of other shake-up features, this transition should start from the $6b_{1g}$ σ orbital having a strong nitrogen-lone-pair character. In a simplified picture, where molecular orbitals are assumed to relax similarly, there is a linear relation between satellite energies and excitation energies of valence electrons. In fact, this relation is not simple, and the orderings of valence excitations and their coresponding satellites can be very different.[23,24] Therefore, it is not unlikely that a satellite of low amplitude may originate in a transition starting from the deep $6b_{1g}$ orbital. However, a more detailed discussion on the nature, the amplitude, and the probability of this transition would need elaborate calculations beyond the scope of this paper.

Further work on compounds with similar NSN linkages is in progress to understand the N 1s peak shape.

Concluding Remarks

The parallel use of X-ray photoelectron spectroscopy and ab initio calculations, undertaken to characterize the electronic structure of $(NSN)_2$, has shown that (i) the nitrogen atoms are negatively charged while sulfurs and carbons linked to nitrogens are positive, (ii) compared to those of naphthalene, the highest occupied levels are strongly perturbed due to the adjunction of two NSN entities, and (iii) C=N has double-bond character, as shown from both shake-up satellites existence and Mulliken population analysis.

These results, in agreement with previous experimental results, suggest the quinonoid structure as the most accurate to describe the bonding in $(NSN)_2$ and $(NSeN)_2$. Sulfur 3d orbitals induce a partial back-donation of electrons from nitrogen to sulfur, thereby reducing the polarity of the NSN bond.

Substitution of sulfur by selenium does not bring any marked modification in the electronic structure, as is reflected by similar HOMO's in $(NSN)_2$ and $(NSeN)_2$.

Registry No. $(NSN)_2$, 65989-13-1; $(NSeN)_2$, 71248-50-5.

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Cadmium-113 NMR T_1 and Nuclear Overhauser Enhancement Measurements on Cadmium Cyclohexanediaminetetraacetate

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Abstract: The ^{113}Cd NMR T_1 and nuclear Overhauser enhancement (NOE) have been measured for CdCyDTA in H_2O and D_2O solutions at 2.3 T. These measurements allowed the calculation of the dipole–dipole contribution to T_1, which was the same in both solutions. A selective NOE experiment was performed on the CdCyDTA solution in 100% H_2O, in which the water protons, the acetate methylene protons, and the methine protons were successively irradiated; only the irradiation of the CyDTA acetate methylene protons gave a detectable NOE. These results demonstrate that water does not penetrate the CdCyDTA inner coordination sphere and that the acetate methylene protons of CyDTA are the only protons which contribute to the dipolar portion of the ^{113}Cd T_1.

Recently considerable interest has been shown in obtaining information about metal-binding sites in zinc, calcium, and other metal-containing proteins via ^{113}Cd NMR of the Cd-substituted proteins.[2-5] As pointed out by Ellis et al.,[6] the study of simpler model systems by ^{113}Cd NMR is necessary in order to better interpret the results obtained on biological systems. The ^{113}Cd relaxation studies on the Cd aquo[7] and CdEDTA[6] complexes are important first steps toward the understanding of ^{113}Cd relaxation

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[†] Deceased December 31, 1981.

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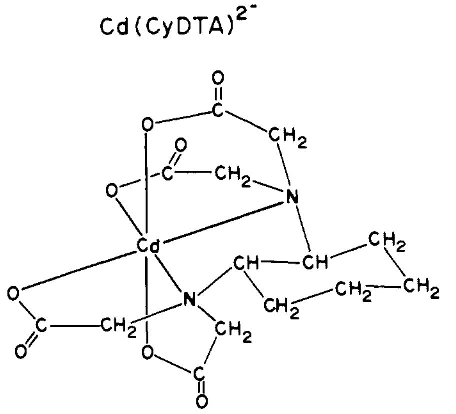

Figure 1. Structure of the CdCyDTA complex.

of Cd complexes in aqueous solution.

The recent T_1 and NOE measurements on CdEDTA[6] were of particular interest to us, as we had performed T_1 and NOE measurements on a related complex, CdCyDTA (CyDTA = cyclohexanediaminetetraacetate) with different results. In aqueous CdEDTA solutions, the dipole–dipole portion of the ^{113}Cd T_1 contained a substantial contribution from water molecules in the Cd^{2+} inner coordination sphere. This result was interpreted as showing that the EDTA ligand was five-coordinate for an appreciable portion of the time, with water occupying the sixth coordination site of Cd^{2+}.

This work shows that there is no detectable H_2O contribution to the dipole–dipole portion of the ^{113}Cd T_1 in aqueous CdCyDTA solutions; consequently water must not be present in the Cd^{2+} inner coordination sphere for any appreciable portion of the time.

Experimental Section

CdCyDTA solutions in H_2O and D_2O were prepared from $Cd(NO_3)_2$ and from H_4CyDTA purchased from the Aldrich Chemical Co. Water (H_2O or D_2O) and NaOH (or NaOD) were added to H_4CyDTA until the ligand was dissolved, and $Cd(NO_3)_2$ was added until nearly all the ligand had reacted, resulting in a solution of about 0.7 M CdCyDTA with a slight excess of free CyDTA. The pH was adjusted to 6.5 with NaOH (or NaOD). Solutions were degassed by bubbling with N_2 and sealing just prior to the NMR experiment.

All ^{113}Cd spectra were obtained at 22.2 MHz on a Varian XL-100/12 NMR spectrometer modified for multinuclear observation,[8] using a Nicolet NT726 18-mm broad-band probe. For each experiment, about 5 mL of solution was placed in an 18-mm NMR tube, and a vortex plug was inserted after degassing. The T_1 measurements were performed by using the $180°-\tau-90°$ pulse sequence, two-pulse rf (radio frequency) phase alternation,[8] and a delay time of 40 s. A set of 8 τ values ranging from 1 to 10 s (except 40 s for τ_∞) was used for each T_1 measurement, with 300 transients averaged for each τ value (36 h total). The T_1 values were determined from a linear least-squares analysis, with an estimated error of ±10%. The ^{113}Cd{^{1}H} NOE measurements were performed by using gated ^{1}H decoupling and a delay time of 100 s. The ^{1}H decoupler was operated at 110 dB without modulation for the selective NOE experiments; otherwise 100-Hz modulation and a decoupler power of 2 W was employed for the NOE and T_1 experiments. The low decoupler power minimized sample heating, with resultant sample temperatures of 35 ± 2 °C.

Results and Discussion

The observation of an NOE for the ^{113}Cd{^{1}H} experiment (Figure 2) demonstrates that protons in the cadmium coordination sphere contribute to the relaxation of the ^{113}Cd nucleus through the dipole–dipole (DD) mechanism. If water is present in the inner coordination sphere, then either the water protons or the ligand protons, or both, could contribute to T_1^{DD}. In order to distinguish between these possibilities, we measured the NOE and the T_1 of ^{113}Cd in 100% H_2O solvent and in 90% D_2O solvent. If water protons contribute significantly to ^{113}Cd relaxation, then T_1^{DD} should be substantially larger for CdCyDTA in the 90% D_2O solution.

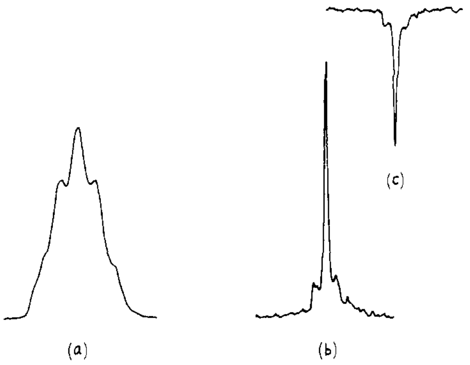

Figure 2. ^{113}Cd NMR spectra of CdCyDTA in 100% H_2O: (a) proton coupled, half-height peak width 56 Hz; (b) proton-decoupled NOE suppressed, half-height peak width 2.5 Hz; (c) proton-decoupled with NOE.

Measurement of the NOE allows the calculation of T_1^{DD} through the relationship

$$T_1^{DD} = \frac{\eta_{max}}{\eta_{obsd}} T_1(\text{obsd}) \qquad (1)$$

where $1 + \eta_{obsd}$ = NOE and $1 + \eta_{max}$ is the NOE which would be observed if the ^{113}Cd relaxation mechanism were entirely dipole–dipole. As Ellis et al.[6] have provided evidence that complexes such as CdEDTA have correlation times which are well within the extreme narrowing limit at 2.3 T, η_{max} is simply $\gamma_H/2\gamma_{Cd} = -2.25$. The ^{113}Cd T_1 and η values for CdCyDTA in 100% H_2O were determined to be 9.8 s and −1.4; inserting these numbers into eq 1 gives $T_1^{DD}(H_2O)$ = 16 s. The T_1 and NOE values in 90% D_2O were 7.2 s and −1.2, giving $T_1^{DD}(D_2O)$ = 14 s. This latter value must be corrected[9] for the greater viscosity of D_2O, which lengthens the correlation time, thus shortening T_1^{DD} With use of 1.18 for the ratio of 90% D_2O to 100% H_2O solvent viscosities, a corrected $T_1^{DD}(D_2O)$ of 16 s is obtained. We see that there is no increase in T_1^{DD} in changing the solvent from 100% H_2O to 90% D_2O solvent; consequently the contribution of water to ^{113}Cd relaxation in aqueous solutions of CdCyDTA must be negligible, and ligand protons must be the only contributors to T_1^{DD}.

To confirm the above conclusion and to determine which ligand protons were most effective in relaxing the ^{113}Cd nucleus, we performed a selective NOE experiment[10] on the CdCyDTA solution in 100% H_2O. The ^{1}H decoupler offset was stepped in 20-Hz increments over a 200-Hz range, with the ^{113}Cd nucleus being observed at each step using low-power (110-dB), single-frequency ^{1}H irradiation. Within the 200-Hz range, the protons of H_2O, the acetate methylene protons, and the ring methine protons were successively irradiated (the proton spectrum has been interpreted by Day and Reilley[11]). When the acetate methylene protons were irradiated, the ^{113}Cd resonance became inverted, but no effect was observed when the water protons or the methine protons were irradiated. The decoupler offset was then set for maximum ^{113}Cd resonance inversion, and an NOE experiment performed with low-power (110-dB), single-frequency ^{1}H irradiation; an η of −1.3 was measured, which is within experimental error of the η measured by using higher power (2-W), square-wave modulated ^{1}H irradiation. Clearly, only the acetate methylene

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protons play a role in relaxing the ^{113}Cd nucleus. This selective NOE experiment also demonstrates that spin diffusion is an ineffective mechanism for transferring spin polarization from the water or methine protons to the acetate methylene protons, as no change in the ^{113}Cd resonance intensity was observed when the water or methine protons were selectively irradiated.

The absence of a dipole–dipole contribution to ^{113}Cd relaxation from water protons in aqueous CdCyDTA solutions is in contrast to the results obtained for CdEDTA solutions[6] and suggests that little or no water is present in the CdCyDTA coordination sphere. Thus the CyDTA ligand must be six-coordinate for virtually all of the time.

Also, the absence of a dipole–dipole contribution to ^{113}Cd relaxation from the methine protons of CyDTA would seem to suggest that the methine protons are significantly farther away from the Cd nucleus than are the acetate methylene protons, as dipolar relaxation has a $1/r^6$ dependence. However, the molecular reorientation motion of CdCyDTA in solution may be anisotropic, in which case the correlation time that governs the ^{113}Cd–^{1}H(methine) dipole–dipole interaction could be different from the correlation time governing the ^{113}Cd–^{1}H(methylene) interaction. It is thus possible that a similar $r_{\mathrm{H-Cd}}$ but a shorter correlation time is responsible for the lack of involvement of the methine protons in the ^{113}Cd T_1^{DD}.

In fact, evidence exists that the methine protons and the axial in-plane acetate methylene protons are closer to the metal center than are other ligand protons; for example, in a ^{1}H NMR study of the paramagnetic NiCyDTA complex, no ^{1}H resonance was observed for either the methine protons or the axial in-plane methylene protons.[12] A reasonable explanation of the failure to observe the resonances is that these protons are closest to the Ni atom and that electron–nuclear dipole–dipole relaxation (which also has a $1/r^6$ dependence) greatly broadened the two types of proton resonances.

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Registry No. CdCyDTA^{2-}, 12607-87-3.

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Electronic Structure of Bis(pentadienyl)iron. Semiempirical Calculations and Photoelectron Spectra[1,2]

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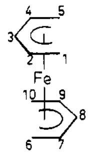
Abstract: The electronic structure of dipentadienyliron (**1**) and its methyl derivatives **2** to **4** has been investigated by means of semiempirical LCAO calculations of the INDO and charge-iterative extended Hückel (EH) types as well as by means of their He I photoelectron (PE) spectra. A significant rotational barrier in the open ferrocenes is predicted, and the origin of the preference of the trans C_{2h} conformation in the gas phase is analyzed. The electronic structure of the bis(pentadienyl) complexes is compared with the nature of bonding in ferrocene and the bis(diene)iron monocarbonyl species. In the open systems a very large degree of metal–ligand coupling and as a result of a larger flexibility of the 3d basis functions a bonding interaction of partial δ character is observed; this behavior is not encountered in ferrocene. In the PE spectra of **2**–**4** two Fe 3d ionization events are predicted on top of the complex HOMO derived from the nonbonding pentadienyl orbitals.

Recently dipentadienyliron (**1**) and several methyl derivatives (e.g., **2**–**4**) have been synthesized.[5] It has been demonstrated that the bis(pentadienyl)iron systems are η^5 complexes with similar iron–carbon distances as in the cyclic counterpart ferrocene (**5**). The electronic structure of the closed sandwich ferrocene has been the subject of various theoretical publications. The degree of sophistication extends from semiempirical calculations of the Wolfsberg–Helmholtz type[6-8] to ab initio calculations of double-ζ quality.[9,10] Quantum chemical studies on bis(pentadienyl) complexes, on the other hand, are missing although various bis(π-allyl) systems theoretically have been analyzed in great detail.[11-13] In connection with our investigations on the dimeric ferrocene species[14] and the bis(diene)iron monocarbonyl systems[15] we be-



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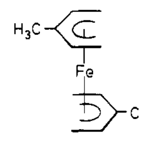

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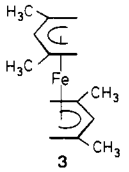

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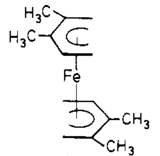

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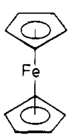

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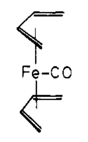

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