cycle, it was clear that $c = 0°$ and $b = 180°$. After the fifth and final cycle, it was certain that $a = d + e$. Thus only symbols d, e, and f remained and could be chosen at will to fix the origin; they were all chosen equal to 0°. The first Fourier synthesis (E map), using 367 reflections with all E's taken as 2.0, clearly showed 23 of the 29 nonhydrogen atoms and several more probable atoms. The subsequent difference Fourier synthesis (electron density difference map) computed from these 23 atoms revealed the remaining 6 carbon atoms as well as indicating moderate shifts in the positions of the 23 input atoms.

Identification of Two Reduction Products of Glyoxal Bis(2-mercaptoanil)nickel. Characterization of the One-Electron Reduction Product and the Partially Hydrogenated Anion

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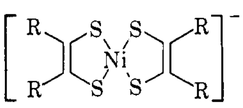
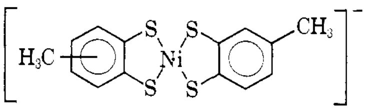
Contribution from the Department of Chemistry, University of California, Riverside, California. *Received January 12, 1967*

Abstract: Two different paramagnetic monoanions have been previously identified as the one-electron reduction product of glyoxal bis(2-mercaptoanil)nickel, Ni(gma). These anions result from (a) the initial borohydride reduction of Ni(gma), and (b) the sodium amalgam reduction of Ni(gma). These ions differ in their physical properties. The ion resulting from (a) has a green color, with $\langle g \rangle = 2.051$, $g_1 = 2.009$, $g_2 = 2.027$, and $g_3 = 2.119$, while the ion resulting from (b) is red-brown, with $\langle g \rangle = 2.0042$, $g_1 = 1.979$, $g_2 = 2.006$, and $g_3 = 2.028$ in 2-methyltetrahydrofuran. In this communication, we demonstrate that the product from (b) is identical in its properties with the one-electron electroreduction product of Ni(gma) in dimethylformamide and, since the reduction wave is reversible, is identified as the monoanion of Ni(gma). The green anion from (a) is shown to result from hydrogen addition across the conjugated bridge and is identified as $Ni(H_2gma)^-$.

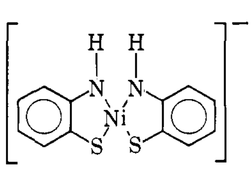
The characterization of stable, square-planar nickel complexes in unusual formal oxidation states has opened an area of discussion concerning their electronic formulation.[2-5] Four types of complexes have played a key role in the discussion and are shown below (I–IV).



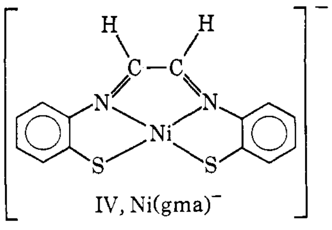
I, R = CN, CF_3, Ph
R = CN, $Ni(mnt)_2^-$



II, $Ni(tdt)_2^-$



III, $Ni(abt)_2^-$



IV, $Ni(gma)^-$

As an example of the problem, the paramagnetic ($S = {}^1/_2$) $Ni(mnt)_2^-$ complex has been described in two different ways: as an effectively d^7 Ni(III) complex, $[Ni^{III}(mnt)_2^{4-}]^-$ [2-5] and as an effectively d^8 Ni(II)-stabilized radical ligand [Ni(II) srl] system, $[Ni^{II}(mnt)_2^{3-}]^-$.[3,4]

In many cases the same polarographic and esr results have been interpreted as supporting the Ni(III) or the Ni(II) srl picture, depending on the relative emphasis placed on various details of these experiments. A particularly unfortunate controversy has arisen concerning the interpretation of polarographic and esr experiments on various reduction products of Ni(gma).[4,5] Specifically, the borohydride[4] and sodium amalgam[5] reduction products are clearly different, and this has led to considerable confusion about the identity of the authentic $Ni(gma)^-$ complex. We have now thoroughly characterized the monoanionic borohydride reduction product of Ni(gma) as a partially hydrogenated species designated $Ni(H_2gma)^-$ (V).

On the other hand, the sodium amalgam reduction product of Ni(gma)[5] has been shown to be the actual anion, $Ni(gma)^-$. These results should give added impetus to the total resolution of the outstanding problems.

It is also our view that in a number of situations the Ni(III) and Ni(II) srl descriptions approach each other. On careful examination of the allegedly opposed formulations,[4,5] it is apparent that there is no significant basis for controversy. Therefore, it is the purpose of this paper to present the characterization of the $Ni(H_2gma)^-$

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(2) A. H. Maki, N. Edelstein, A. Davison, and R. H. Holm, *J. Am. Chem. Soc.*, **86**, 4580 (1964).

(3) S. I. Shupack, E. Billig, R. J. H. Clark, R. Williams, and H. B. Gray, *ibid.*, **86**, 4594 (1964).

(4) E. I. Stiefel, J. H. Waters, E. Billig, and H. B. Gray, *ibid.*, **87**, 3016 (1965). The complex referred to as $Ni(gma)^-$ in the esr work in this communication is probably $Ni(H_2gma)^-$.

(5) A. H. Maki, T. E. Berry, A. Davison, R. H. Holm, and A. L. Balch, *ibid.*, **88**, 1080 (1966).

and Ni(gma)$^-$ complexes and to attempt to resolve as many of the controversial electronic structural issues as possible.

Experimental Section

Preparation of (*n*-Bu$_4$N)[Ni(H$_2$gma)] from (*n*-Bu$_4$N)(BH$_4$) and Ni(gma). All solvents used in this synthesis were degassed by four cycles of freezing and drying on the high-vacuum line unless noted otherwise. All operations were conducted in the drybox in a dry nitrogen atmosphere. Ethanol used was USP Grade Absolute. The THF was dried (prior to degassing) by distilling from LiAlH$_4$ under N$_2$.

We suspended Ni(gma), (0.8 g, 0.0024 mole) in 150 ml of THF, and a solution of (*n*-Bu$_4$N)(BH$_4$) (1.4 g, 0.0054 mole) in 50 ml of THF was added. The Ni(gma) rapidly dissolved, giving a green solution. A sample withdrawn at this stage in a flat quartz cell for esr measurement revealed the presence of two signals. The stronger had $\langle g \rangle = 2.004$, while the other had $\langle g \rangle = 2.048$. These signals were observed to decay in intensity while in the spectrometer. An esr measurement was made initially before the decay was observed. Comparison with the signal intensity of a standard (Et$_4$N)[Ni(mnt)$_2$] solution revealed that the spin concentration in the two signals could account only for about 6% of the Ni atoms in the reaction solution. A second sample withdrawn from the reaction mixture after 0.5 hr of stirring showed no trace of esr absorption near $\langle g \rangle = 2$.

A solution of 1.0 g of (*n*-Bu$_4$N)Br in 150 ml of absolute EtOH was added, resulting in an immediate discharge of the green color and evolution of gas. A sample of the grayish black solution showed no esr absorption. We next bubbled a small quantity of dry O$_2$ into the solution. A brilliant green color was observed to form immediately and increased in intensity as more O$_2$ was added. Monitoring the solution with esr indicated that the formation of the green color was associated with the development of an intense signal with $\langle g \rangle = 2.047$. An intensity measurement gave the number of spins in the line equivalent to 81 ± 10% of the number of Ni atoms in the reaction mixture. Addition of excess O$_2$ to a small portion of the reaction mixture resulted in a decrease in the intensity of the line at $\langle g \rangle = 2.047$ and the development of a new signal at $\langle g \rangle = 2.0043$.

Green, microcrystalline (*n*-Bu$_4$N)[Ni(H$_2$gma)] was obtained by evaporating the O$_2$-treated mixture to about half its volume and diluting with a large volume of *n*-hexane (Matheson Coleman and Bell Spectroquality, not degassed). The precipitate was washed with hexane and dried *in vacuo* over P$_2$O$_5$. The infrared spectrum of this solid was recorded as mulls in Nujol and Fluorolube.

Several acceptable analyses on samples from different preparations of (*n*-Bu$_4$N)[Ni(H$_2$gma)] were obtained. The best analysis is given here.

Anal. Calcd for (*n*-Bu$_4$N)[Ni(H$_2$gma)]: C, 62.81; H, 8.45; N, 7.33; S, 11.18. Found: C, 62.56; H, 8.56; N, 7.25; S, 11.10.

Preparation of (*n*-Bu$_4$H)[Ni(HDgma)] from (*n*-Bu$_4$N)(BD$_4$) and Ni(gma). We prepared the complex as described above, using (*n*-Bu$_4$N)(BD$_4$) instead of (*n*-Bu$_4$N)(BH$_4$). An infrared spectrum of (*n*-Bu$_4$N)[Ni(HDgma)] as a Fluorolube mull when compared with that of (*n*-Bu$_4$N)[Ni(H$_2$gma)] prepared with (*n*-Bu$_4$N)(BH$_4$) showed the absence of one of the weak C–H stretching bands (at 2820 cm^{-1}) and the presence of a new band at 2130 cm^{-1} attributable to C–D stretching indicating the incorporation of at least one D atom into the gma structure. Neither sample showed the presence of a band attributable to an N–H stretching vibration.

A sample of (*n*-Bu$_4$N)[Ni(HDgma)] prepared with (*n*-Bu$_4$N)(BD$_4$) was completely burned in O$_2$, the water of combustion was collected and frozen, all volatiles were pumped off *in vacuo*, and the sample was introduced into a mass spectrometer. The ratio of peak heights HOD/H$_2$O was determined. The calculated ratio (corrected for natural abundance of D) for one D atom/mole is 0.043, and for two D atoms/mole is 0.088. Two successive determinations yielded 0.043 and 0.044, establishing unequivocally that the reduction of Ni(gma) with BD$_4$$^-$ involves the incorporation of one deuterium atom per molecule of Ni(gma).

Preparation of (*n*-Bu$_4$N)[Ni(gma)]. All solvents were dried and degassed as described in an earlier section, and all operations were carrried out in a drybox.

Ni(gma) (3.29 g, 0.01 mole) was suspended in 50 ml of THF and treated with 0.20 g (0.0087 g-atom) of sodium in 20 ml of Hg. The complex dissolved rapidly on shaking to form a deep red-brown solution.

Addition of 3.22 g of (*n*-Bu$_4$N)Br in 100 ml of ethanol to the filtered solution gave a brown crystalline precipitate which was filtered and dried *in vacuo* over P$_2$O$_5$. The (*n*-Bu$_4$N)[Ni(gma)] is extremely air sensitive and must be handled in an inert atmosphere.

Anal. Calcd for (*n*-Bu$_4$N)[Ni(gma)]: C, 63.05; H, 8.11; N, 7.35; S, 11.22. Found: C, 61.93, 61.83; H, 7.65, 7.83; N, 7.22, 7.07; S, 11.36, 11.55.

Physical Measurements. Static susceptibility measurements on solid samples were made at room temperature by the Gouy method using Hg[Co(SCN)$_4$] as calibrant.[6] Conductances were determined on an Industrial Instruments bridge, Model RC16B2, using a cell calibrated with 0.02 *M* KCl solution. Polarographic measurements were made in DMF solution with a dme in a three-electrode cell, using an electronic polarograph described elsewhere.[7] Silver-silver perchlorate was used as the reference electrode (Ag|AgClO$_4$, 0.1 *M;* (*n*-Pr$_4$N)ClO$_4$, 0.1 *M*). Solutions were approximately 10^{-3} *M* in complex and 10^{-1} *M* in (*n*-Pr$_4$N)ClO$_4$. Cyclic voltammetry was employed, using a platinum indicator electrode and a Ag|AgCl(1.0 *M* KCl) reference electrode. The same electrodes and scan rates were used for all comparative measurements. The DMF solvent for cyclic voltammetry and epr measurements was Baker Analyzed reagent, gc-spectrophotometric quality that had been fractionated under vacuum from K$_2$CO$_3$ on a spinning-band column and stored in the drybox until used. Sample preparation, cyclic voltammetry measurements, and the filling of epr sample cells were all done within the drybox. Solutions were about 10^{-1} *M* in *n*-Bu$_4$NClO$_4$ and 5×10^{-4} *M* in complex unless otherwise stated. Optical spectra were measured on a Cary Model 14 spectrophotometer in the wavelength range 350–700 mμ. Esr measurements were made on a Varian V-4502-12 spectrometer system operating at 9500 Mc/sec using 100-kc/sec field modulation. The microwave frequency was measured by means of a Hewlett-Packard Model 2590A frequency converter and Model 5245L frequency counter. The magnetic field was monitored with a proton resonance gaussmeter whose frequency was measured by the same frequency counter. $\langle g \rangle$ values were calculated by means of the equation[8]

$$g = 3.041997 \times 10^{-3}\nu_l/\nu_p$$

Results

The green crystalline (*n*-Bu$_4$N)[Ni(H$_2$gma)] complex is a 1:1 electrolyte in nitromethane ($\Lambda = 64$). The esr spectrum of a polycrystalline sample of (*n*-Bu$_4$N)[Ni(H$_2$gma)] shows three g values. The average $\langle g \rangle$ estimated from the polycrystalline spectrum is 2.050 ± 0.005. The esr spectra in various carefully prepared solutions (under oxygen-free nitrogen from freshly distilled and degassed solvents), with DMF, DMSO, and THF as solvents, show $\langle g \rangle$ values in a small range near 2.051, with the lowest vaue being 2.048 ± 0.002 in THF solution. The complex has a magnetic moment of 1.95 BM in the solid state, in good agreement with the $\langle g \rangle$ value of 2.050 from the esr spectrum of a polycrystalline sample. In DMF–CHCl$_3$ the Ni(H$_2$gma)$^-$ ion has the following g values in the low-temperature glass:[9] $g_1 = 2.009$, $g_2 = 2.027$, $g_3 = 2.119$. The (*n*-Bu$_4$N)[Ni(H$_2$gma)] complex in DMF solution shows a reversible one-electron oxidation wave at −0.758 v and a reversible one-electron reduction wave at −1.591 v *vs.* Ag|AgClO$_4$. Under identical solvent and instrumental conditions, a pure sample of neutral Ni(gma) shows reversible one-electron reduction waves at −0.823 and −1.605 v. These differences in half-wave potentials for the Ni(gma) and Ni(H$_2$gma)$^-$ systems are small, but are definitely outside of experimental error.

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[6] B. N. Figgis and J. Lewis, "Modern Coordination Chemistry," Interscience Publishers, Inc., New York, N. Y., 1960, p 406.

[7] M. J. Kelley, J. D. Fisher, and K. C. Jones, *Anal. Chem.*, **31**, 1475 (1959); **32**, 1262 (1960).

[8] B. G. Segal, M. Kaplan, and G. K. Fraenkel, *J. Chem. Phys.*, **43**, 4191 (1965).

[9] Z. Dori, E. I. Stiefel, R. Eisenberg, and H. B. Gray, to be published.

The (n-Bu$_4$N)[Ni(H$_2$gma)] complex is air sensitive (as would be expected from the polarographic results), and all operations which preserve its properties must be carried out under nitrogen. Upon exposure to air in any solvent the green color rapidly fades and a brown color develops. The compound is apparently being oxidized by air, but a pure sample of either Ni(H$_2$gma) or Ni(gma) could not be isolated by this route. A freshly prepared sample of analytically pure (n-Bu$_4$N)-[Ni(H$_2$gma)] was dissolved in freshly distilled THF under N$_2$, giving a single strong signal at $\langle g \rangle = 2.048$. The sample was then allowed to stand in air until it appeared brownish. The signal at $\langle g \rangle = 2.048$ was still present but with greatly reduced intensity. In addition, a new and strong signal appeared at 2.004. An analogous experiment was then performed in DMF solution in the polarographic cell. After the brown color appeared, no reversible waves could be found, even when the cell was reflushed with nitrogen. The nature of the reaction product with $\langle g \rangle = 2.004$ is still uncertain. This paramagnetic species is not the same as Ni(gma)$^-$, resulting from the coulometric reduction of Ni(gma), although its $\langle g \rangle$ value is similar (*vide infra*).

Further confirmation of the identity of Ni(H$_2$gma)$^-$ is provided by preliminary work on the crystal structure of the borohydride reduction product of dimethylglyoxal bis(2-mercaptoanil)nickel. It is found that the CH$_3$–C–C–CH$_3$ angles are consistent with a tetrahedral configuration around at least one of the carbon atoms in the bridge.[9]

Cyclic voltammetry measurements of Ni(gma) in DMF gave a one-electron reduction wave (checked by coulometry) with a peak potential of -0.322 v and an oxidation peak at -0.253 v *vs.* Ag|AgCl on the reverse scan. The accuracy of these and subsequent values is estimated at ±0.003, unless otherwise stated, and was obtained as the average of two successive scans. Complete coulometric reduction of this solution was carried out at a constant potential of -0.5 v. Cyclic scans of this solution showed a reduction peak at -0.320 v and an oxidation peak at -0.250 v *vs.* Ag|AgCl. This agreement of potentials leaves little doubt that the product of this electroreduction of Ni(gma) is Ni(gma)$^-$. Cyclic voltammetry measurements on the sodium amalgam reduction product of Ni(gma)[5] (as the analyzed n-Bu$_4$N$^+$ salt) showed a reduction peak at -0.321 v and an oxidation peak at -0.250 v *vs.* Ag|AgCl in excellent agreement with Ni(gma) and Ni(gma)$^-$ prepared by coulometric reduction. Cyclic voltammetry of (n-Bu$_4$N)[Ni(H$_2$gma)] showed a reduction peak at -0.226 v and an oxidation peak at -0.146 v *vs.* Ag|AgCl. These potentials are well outside of experimental error of the Ni(gma) potentials, as are the polarographic half-wave potentials reported above.

The second reduction peaks of Ni(gma) and (n-Bu$_4$N)-[Ni(gma)] (sodium amalgam reduced) were also compared by sweeping both reduction peaks in the same scan. The second reduction and oxidation peaks occurred at -1.112 and -1.031 v for Ni(gma), and -1.097 and -1.036 v *vs.* Ag|AgCl for (n-Bu$_4$N)[Ni(gma)]. The estimated accuracy in this case is ±0.005 v because of the larger voltage scan. These solutions were about 3×10^{-3} M in complex.

In order further to confirm the identity of the sodium amalgam reduced Ni(gma) and coulometrically generated Ni(gma)$^-$, we have made an accurate *comparison* of the $\langle g \rangle$ values of the two paramagnetic ions in DMF. The coulometrically reduced Ni(gma)$^-$ solution contained 0.1 M (n-Bu$_4$N)ClO$_4$ as supporting electrolyte. In order to avoid possible ionic strength effects on $\langle g \rangle$ values, the solution of the sodium amalgam reduced salt was also made up to 0.1 M in (n-Bu$_4$N)ClO$_4$. With samples having $\langle g \rangle$ near the free spin value, the utmost precision must be employed to use this quantity as a qualitative analytical tool. This is because the region near $\langle g \rangle = 2.0023$ is thoroughly uncharacteristic, a large number of paramagnetic systems, including almost all of those described as free radicals, falling into this region. The principal uncertainty in our determination of *absolute* $\langle g \rangle$ values results from the difference in magnetic field at the sample and at the proton resonance probe, which must necessarily be placed in a different region of the magnetic pole gap. In order to avoid this error, we chose to measure the *difference* in $\langle g \rangle$ values of the two samples. Each sample was placed in a separate Varian flat cell, and the $\langle g \rangle$ value of each determined in turn in the same rectangular microwave cavity. The locations of the cavity and proton probe were disturbed as little as possible between the pair of determinations. The magnetic field was left on during a pair of determinations to avoid the small error due to a change in the field *difference* between sample and proton probe locations which is known to occur if the magnetic field is disturbed.[8] Six pairs of determinations were made over a period of 3 days. In three of these the sample cells were exchanged to avoid any possible systematic error arising from this source.

The $\langle g \rangle$ values obtained from the six determinations were 2.004025 ± 0.000012 for coulometrically reduced Ni(gma) and 2.004052 ± 0.000012 for sodium amalgam reduced Ni(gma). It should be emphasized that these $\langle g \rangle$ values are not known *absolutely* to the precision quoted above, since no correction has been made for the systematic field difference between sample and proton probe locations. The estimate of precision applies when the two values are compared. We conclude that we cannot distinguish between the $\langle g \rangle$ values of the two samples within the precision of the determination. An evaluation of the absolute $\langle g \rangle$ value of both samples gives $\langle g \rangle = 2.0041 \pm 0.0001$. We previously reported[5] $\langle g \rangle = 2.0527$ for coulometrically reduced Ni(gma) in CHCl$_3$–DMF. We now believe that the radical generated in this experiment resulted from a reaction product of Ni(gma) with impurities present in DMF; the radical is possibly III or V. This result emphasizes the extreme care which must be exercised when working with these systems. Scrupulously purified DMF leads only to Ni(gma)$^-$ on electroreduction, as reported above.[10]

Optical absorption spectra of coulometrically reduced and sodium amalgam reduced Ni(gma) in DMF were identical in the observed region, 350–700 mμ. Concentrations were about 10^{-4} M. Extinction coefficients were not measured. The main features of both spectra in this wavelength region are a strong absorption at 444 mμ which has three weak shoulders at 483, 503, and 539 mμ. A second, weaker absorption occurs at 589 mμ.

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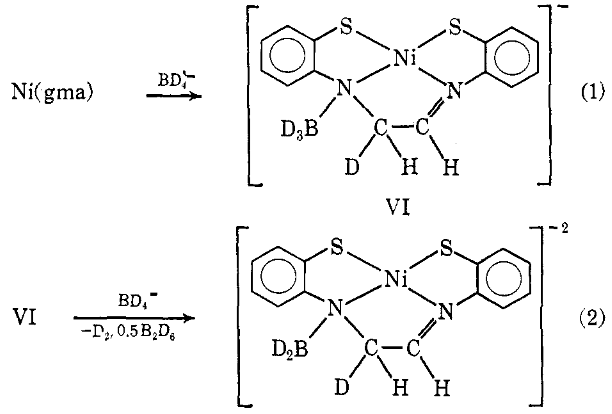
(10) Although Ni(gma)$^-$ is stable for at least a week in scrupulously purified DMF, it undergoes decomposition within 5 days in the impure solvent leading to three new esr signals as reported in ref 5.

On the basis of the voltammetric measurements, esr, and the similarity of the optical spectra, we conclude that the sodium amalgam reduced Ni(gma) is correctly identified as Ni(gma)$^-$.

Discussion

A Possible Reaction Sequence for the Synthesis of Ni(H$_2$gma)$^-$. The data presented above show that borohydride reduction of Ni(gma) followed by treatment with a protic solvent and partial air oxidation leads to a substantial yield of the green complex designated as Ni(H$_2$gma)$^-$, an anion in which the bridge is partially saturated. Substitution of borodeuteride in the reaction gives a product which must be formulated as Ni(HDgma)$^-$. The infrared spectral evidence favors a C–D bond. A reaction sequence which is consistent with all of our observations may be formulated as shown in eq 1–4.



VI

VII

$$\text{VII} \xrightarrow[-\text{B(OEt)}_3,\ 2\text{HD}]{3\text{EtOH}} \text{Ni(HDgma)}^{-2} \qquad (3)$$

$$\text{Ni(HDgma)}^{-2} \xrightarrow{\text{O}_2} \text{V} \qquad (4)$$

Ground-State Electronic Structure. One of the most interesting and desirable features to know in the monoanionic complexes such as Ni(mnt)$_2^-$ and Ni(gma)$^-$ is the distribution of the unpaired electron between the metal and the ligand atoms. The Ni(II) srl and Ni(III) electronic structural formalisms imply different distributions for this unpaired electron. In the former case the unpaired electron is assumed to be in a molecular orbital of predominantly ligand composition, but metal d orbital participation is an important, if secondary, feature.[3,4] That is, the term "Ni(II) stabilized" is meant to imply specific d orbital involvement in the appropriate molecular orbital, even though the ligands dominate in the electron distribution. The second point of view has been traditional when trying to describe the electron paramagnetic properties of "covalent" transition metal complexes. It begins from an appropriate d-orbital configuration on the metal and subsequently allows for mixing of metal and ligand orbitals of the appropriate symmetry. It is clear that properties of paramagnetic transition metal complexes which depend upon the electron spin density near the metal atom (such as electron–metal nucleus hyperfine interaction, as well as large deviations of the g tensor from that of the free electron spin) are better handled from this point of view. The two viewpoints are, of course, complementary and fuse together in those complexes having roughly an equal distribution of spin density between metal and ligand orbitals.

Electron paramagnetic resonance should be of perhaps the greatest use in helping to decide matters of electron spin distribution in paramagnetic $S = {}^1/_2$ complexes such as I–V. Particularly helpful would be the measurement of the anisotropic dipole–dipole contribution to the electron–metal nucleus hyperfine tensor. Since this property depends mostly on the ground state electron configuration, and to a much smaller extent on admixture of excited configurations through spin–orbit coupling (unless the g anisotropy is very large), it is most *directly* indicative of the wave function of the half-filled orbital in a molecular orbital description. The g tensor, on the other hand, depends not only on the ground-state configurational wave function, but on all the excited configurational wave functions and their degree of admixture by spin–orbit coupling. Measurement of the g-tensor is thus not as *directly useful* in leading to a quantitative description of the half-filled orbital, within the framework of existing molecular theory.

In the series of complexes under discussion, metal nucleus–electron hyperfine interaction thus far only has been measured for I, R = CN, using a sample enriched in ^{61}Ni. The hyperfine tensor was interpreted to result from a ground-state configuration in which the half-filled b$_{3g}$ orbital was approximately 50% delocalized over the ligand π system.[2,11] This interpretation places Ni(mnt)$_2^-$ directly in the overlap region between the two extreme descriptions (*vide supra*) of these complexes.

Care should be exercised in interpreting the g-tensor anisotropy in terms of the lowest energy configuration. This can be done only in the roughest, most qualitative way in this series of square-planar Ni complexes in the absence of detailed calculations and an adequate theory. Perhaps all that can be done at present is to define the behavior of the magnetic properties of the complex in the two extreme limits. In the limit of the d^7 model, Ni(III), we would expect a metal nucleus–electron hyperfine tensor which is consistent with the value of r^{-3} given by a calculation on a properly self-consistent metal d orbital. In the limit of the Ni(II) srl model we would expect a very small anisotropy of the metal hyperfine tensor, as well as a g tensor which approaches that characteristic of the isolated ligand free radical.

Acknowledgment. We wish to thank Dr. Donald Young for mass spectral analyses. This project was partially supported by grants from the National Science Foundation (GP-3398, GP-4922, and GT623-IX).

(11) This symmetry for the half-filled orbital also has been obtained by a MO calculation: G. N. Schrauzer and V. P. Mayweg, *J. Am. Chem. Soc.*, **87**, 3585 (1965).