

Crystal and Molecular Structure of the Tetraethylammonium Salt of Diacetyldihydrobis(2-mercaptoanil)nickel Monoanion

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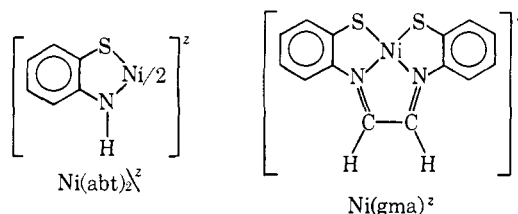
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Abstract: The crystal and molecular structure of the complex tetraethylammonium diacetyldihydrobis(2-mercaptoanil)nickelate, $[\text{Et}_4\text{N}][\text{Ni}(\text{H}_2\text{dma})]$, has been determined from three-dimensional single-crystal X-ray data collected by standard film techniques. The structure has been refined by least-squares methods to a conventional R factor of 0.108 for 1551 nonzero reflections. The compound crystallizes in space group $\text{P}2_1/c$ (C_{2h}^5) of the monoclinic system, with a cell of dimensions $a = 7.61 \pm 0.02$, $b = 17.11 \pm 0.02$, $c = 18.81 \pm 0.02$ Å, $\beta = 101.4 \pm 0.4^\circ$, $V = 2402$ Å³. An experimental density of 1.33 ± 0.02 g/cm³ is in good agreement with a calculated value of 1.32 g/cm³ for four molecules in the unit cell. The Et_4N^+ cation has its expected tetrahedral geometry about the nitrogen. The S_2N_2 coordination about the nickel is nearly planar, but the anion as a whole is distorted with both benzene rings tilted out of the coordination plane of the anion in the same direction. The orientation of the two methyl groups with respect to the NCCN bridge indicates that the α -diimine linkage has been hydrogenated in this complex, and that one hydrogen is attached to each of the two carbon atoms. The interesting bond length data are compatible with a coordinated radical-ligand model of electronic structure.

Recent work has provided a large number of examples of four-coordinate nickel complexes with a spin-doublet ground state.^{2,3} The complexes investigated to date contain two five-membered chelate rings, generally with sulfur donor atoms. One of the important electronic structural problems in these systems concerns the definition of the molecular orbital containing the unpaired electron. Ideally, we should like to ascertain both the metal/ligand composition and the symmetry of the orbital. A related problem, still largely unresolved, is the state of oxidation of the ligands and the central metal atom in these complexes.

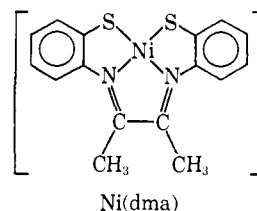
Noteworthy of the efforts toward electronic structural elucidation of these systems is a single crystal esr investigation which has established that the molecular orbital containing the unpaired electron in bis(maleonitriledithiolene)nickel monoanion has at least 50% ligand character.⁴ It is clear that when an orbital is close to 50% metal and 50% ligand character, it is not meaningful to assign this orbital to either the metal or the ligand for the purpose of oxidation state designation. One might even question the efficacy of using an oxidation state at all in these cases. Nevertheless, we believe that a knowledge of the structural and electronic properties of the complex can very often lead to a consistent formulation.

Our recent efforts to probe such electronic structural matters have focused on the $\text{Ni}(\text{abt})_2^{\cdot-}$ and $\text{Ni}(\text{gma})^{\cdot-}$ systems.⁵ In the course of this work we have prepared, quite accidentally, and characterized the interesting spin-doublet complex $\text{Ni}(\text{H}_2\text{gma})^-$. The complex $\text{Ni}(\text{H}_2$



$\text{gma})^-$ assumes a key role in the electronic structural discussions, because its polarographic and esr properties are essentially identical with those of $\text{Ni}(\text{abt})_2^{\cdot-}$. Although there is good evidence⁶ that $\text{Ni}(\text{H}_2\text{gma})^-$ is the bridge-saturated derivative of $\text{Ni}(\text{gma})^-$, direct structural confirmation is obviously very desirable.

In order to elucidate the structure of the $\text{Ni}(\text{H}_2\text{gma})^-$ complex, we have undertaken the preparation and full structural characterization of the related complex diacetyldihydrobis(2-mercaptoanil)nickel monoanion $\text{Ni}(\text{H}_2\text{dma})^-$. The parent compound in this series is the dimethyl derivative of $\text{Ni}(\text{gma})$, called $\text{Ni}(\text{dma})$.



The results of this investigation and their relevance to the electronic structural questions are presented in this paper.

Experimental Section

Preparation of $\text{Ni}(\text{dma})$.⁷ Diacetylbis(2-mercaptoanil) (1 g) was dissolved in 500 ml of boiling methanol. Nickel acetate

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(7) This was prepared by the method of H. Jadamus, Q. Fernando, and H. Fieser, *ibid.*, **86**, 3056 (1964).

Table I. Final Parameters for [Et₄N][Ni(H₂dma)]. Final Positional and Isotropic Thermal Parameters

Atom	x	y	z	B, Å ²
Ni	0.0599(2)	0.1860(2) ^a	-0.1173(2)	4.8(1) ^b
S ₁	-0.0564(3)	0.2754(2)	0.0616(2)	6.0(1) ^b
S ₂	-0.1882(2)	0.1472(3)	-0.1830(2)	5.9(1) ^b
N ₁	0.279(2)	0.220(2)	-0.070(1)	4.7(2)
N ₂	0.175(2)	0.120(1)	-0.169(1)	4.2(3)
EC ₁	0.439(1)	0.178(2)	-0.088(1)	4.2(3)
EC ₂	0.367(1)	0.109(2)	-0.141(2)	5.1(3)
EM ₁	0.566(2)	0.151(1)	-0.015(1)	6.1(4)
EM ₂	0.391(1)	0.024(2)	-0.101(1)	6.4(4)
R ₁ C ₁	0.299(1)	0.291(1)	-0.037(2)	4.9(3)
R ₁ C ₂	0.471(2)	0.330(1)	-0.015(1)	4.7(3)
R ₁ C ₃	0.468(1)	0.402(2)	0.019(1)	6.1(4)
R ₁ C ₄	0.310(2)	0.432(1)	0.038(1)	5.8(4)
R ₁ C ₅	0.142(1)	0.395(1)	0.015(1)	6.1(4)
R ₁ C ₆	0.140(1)	0.324(1)	-0.023(2)	4.8(3)
R ₂ C ₁	0.084(1)	0.079(1)	-0.227(1)	4.9(3)
R ₂ C ₂	0.173(1)	0.028(2)	-0.270(1)	5.9(4)
R ₂ C ₃	0.049(1)	-0.009(1)	-0.329(1)	6.0(4)
R ₂ C ₄	-0.131(2)	0.004(1)	-0.346(1)	6.3(4)
R ₂ C ₅	-0.209(1)	0.052(2)	-0.303(1)	6.0(4)
R ₂ C ₆	-0.101(1)	0.091(1)	-0.241(1)	4.9(4)
EtN	0.191(1)	0.172(1)	0.181(1)	5.3(3)
Et ₁ C ₁	0.076(2)	0.076(1)	0.074(1)	7.5(4)
Et ₁ C ₂	-0.136(2)	0.186(1)	0.191(1)	9.6(5)
Et ₂ C ₁	0.397(2)	0.287(1)	0.172(1)	7.4(4)
Et ₂ C ₂	0.441(1)	0.134(1)	0.288(1)	7.1(4)
Et ₃ C ₁	0.152(2)	0.086(1)	0.157(1)	9.2(5)
Et ₃ C ₂	0.328(2)	0.205(1)	0.142(1)	8.4(5)
Et ₄ C ₁	0.255(2)	0.171(1)	0.265(1)	8.4(5)
Et ₄ C ₂	0.017(3)	0.224(1)	0.162(1)	10.4(6)

Final Anisotropic Thermal Parameters						
Atom	β ₁₁ ^c	β ₂₂	β ₃₃	β ₁₂	β ₁₃	β ₂₃
Ni	0.0211(5)	0.0039(1)	0.0037(1)	-0.0002(2)	0.0018(1)	0.0001(1)
S ₁	0.0226(5)	0.0050(2)	0.0053(2)	0.0002(3)	0.0036(3)	-0.0005(1)
S ₂	0.0219(6)	0.0052(2)	0.0048(2)	0.0003(3)	0.0014(3)	-0.0004(1)

^a The estimated standard deviation in the least significant figure is given in parentheses. ^b From the isotropic refinement. ^c The general form for the anisotropic temperature factor is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

(1 g) in 150 ml of methanol was then added dropwise to the boiling solution over a period of 2 hr. The boiling was continued for 15 min and then the hot solution was allowed to cool to room temperature. Filtration yielded shiny flakes of Ni(dma) which were washed with methanol and ether and dried under vacuum overnight. *Anal.* Calcd for Ni(dma): C, 53.81; H, 3.96; N, 3.85; S, 17.45. Found: C, 53.71; H, 3.73; N, 3.93; S, 17.69.

Preparation of [Et₄N][Ni(H₂dma)]. Ni(dma) (0.8 g) was suspended in 150 ml of purified THF (distilled from LiAlH₄), and N₂ was bubbled through the suspension for 2 hr. A solution of (Et₄N)-BH₄ (1.4 g) in 50 ml of THF was added to the suspension, giving an intense green color. A 150 ml solution of (Et₄N)Br (1.0 g) in absolute ethanol was added. After continuation of the N₂ bubbling for 1 hr, the solution was filtered in air. With all succeeding operations carried out under nitrogen, the filtrate was stripped to 200 ml and 150 ml of absolute ethanol was added. The green crystals which precipitated were washed with 200 ml of absolute ethanol and 200 ml of ethyl ether and dried under vacuum for 5 hr. *Anal.* Calcd for [Et₄N][Ni(H₂dma)]: 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 the Crystal. Crystals suitable for the X-ray investigation were prepared as follows. All operations were carried out under nitrogen atmosphere, and all solvents were carefully degassed before use. The complex was dissolved in a 4:1 mixture of THF and 1-butanol. An evaporating dish containing the above solution was placed in a large desiccator which was filled with THF up to the support plate. The desiccator was then connected to an aspirator and light suction was applied. Green crystals suitable for X-ray work were formed after a period of about 4 days. The crystals were filtered, washed with ethanol and dry ether, and then dried *in vacuo*. A small crystal (0.08 × 0.08 × 0.1 mm) was chosen, sealed under nitrogen in a thin capillary tube, and mounted on a goniometer head.

Collection of X-Ray Data. Optical goniometry, precession, and Weissenberg photographs showed that the crystals belong to the monoclinic system with a cell of dimensions $a = 7.61 \pm 0.02$, b

$= 17.11 \pm 0.02$, $c = 18.81 \pm 0.02$ Å, $\beta = 101.4 \pm 0.4^\circ$, $V = 2402$ Å³. The observed extinctions $0k0$ for k odd and $h0l$ for l odd are consistent with the unique space group P2₁/c. An experimental density of 1.33 ± 0.02 g/cm³ obtained by flotation in benzene-CCl₄ solutions agrees well with the calculated value of 1.32 g/cm³ for four molecules in the unit cell.

Intensity data were collected by the equiinclination Weissenberg technique. Preliminary Weissenberg photographs of the layers $0kl$ to $6kl$ were recorded using Zr-filtered Mo K α radiation. Although the photographs were of good quality, it was apparent that an insufficient number of nonzero reflections were present for a reasonably high ratio of observations to parameters in a complete structure determination. A set of intensity data was therefore collected using Ni-filtered Cu K α radiation. The layers of $0kl$ and $5kl$ were recorded on multiple films and the intensities of 2099 independent reflections accessible within the angular range $\theta_{Cu} \leq 60^\circ$ were estimated visually using a calibrated intensity strip. The films were interleaved with black paper so as to obtain film factors in the range 2.5–3.5. Very few reflections were observed above the angular limit of $\theta_{Cu} \leq 60^\circ$. The usual Lorentz polarization factors were then applied to these intensities to yield F_o^2 values, where F_o is the observed structure factor amplitude. Because of the very small dimensions of the crystal and the low linear absorption coefficient ($\mu = 26.8$ cm⁻¹), no absorption correction was applied to the data. The F_o values were subsequently brought to an approximate absolute scale through a modification of Wilson's procedure.

Solution and Refinement of the Structure. Using the first set of data, the positions of the Ni and two S atoms were determined from a three-dimensional Patterson function.⁸ The positional parameters of the Ni and the two S atoms, along with variable isotropic temperature factors assigned to them, were refined through two

(8) The main programs for the IBM 7094 computer used in this work were local modifications of Zalkin's *FORDAP* Fourier program and the Busing-Levy *ORFLS* least-squares program. C. K. Johnson's *ORTEP* thermal ellipsoid plotting program was used for the illustrations.

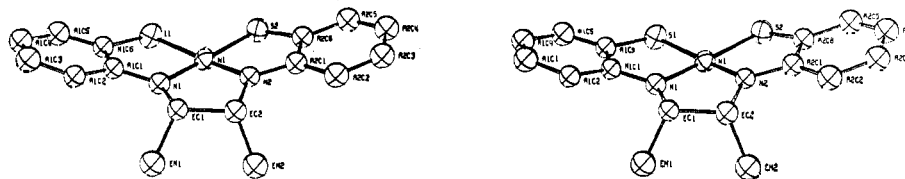


Figure 1. A perspective drawing of the NiH_2dma^- anion. These drawings constitute a stereo pair and may be viewed with a hand viewer.

two S atoms were allowed to vibrate anisotropically. The final refinement converged to an R value of 0.108 and R' of 0.107. The weighting scheme yielded a value of 2.4 for the estimated standard deviation of an observation of unit weight. A final difference Fourier map showed no peaks higher than $0.5 \text{ e}/\text{\AA}^3$ (about 20% the height of a C atom), and at this point the structure determination was considered complete. Attempts to locate both of the ethylene hydrogen atoms with *complete certainty* were unsuccessful. Although approximate positions were determined for a number of the hydrogen atoms in the structure, their contributions to $|F_o|$ were not included in any further calculations.

Table I contains the final parameters obtained from the calculations in which the Ni and the two S atoms were allowed to vibrate anisotropically. The final values of observed and calculated structure factors are listed in Table II.

Description of the Structure. Figure 1 shows a stereo view of an isolated complex. All important intramolecular distances and angles are given for the complex in Table III. The crystal structure of the complex consists of the packing of discrete Et_4N^+ cations and approximately planar $\text{Ni}(\text{H}_2\text{dma})^-$ anions. The anions are well separated, the closest Ni-Ni distance being 7.9 Å. All intermolecular contacts appear normal.

Table III. Principal Intramolecular Bond Distances and Bond Angles for $[\text{Et}_4\text{N}][\text{NiH}_2\text{dma}]$

Distance, Å		Angle, deg	
Anion			
Ni-S ₁ ^a	2.140(2) ^b	S ₁ -Ni-N ₁	87.6(3)
Ni-S ₂	2.151(2)	S ₂ -Ni-N ₂	87.9(2)
Ni-N ₁	1.83(1)	S ₁ -Ni-S ₂	95.8(3)
Ni-N ₂	1.81(1)	N ₁ -Ni-N ₂	88.1(3)
N ₁ -EC ₁	1.50(2)	Ni-S ₁ -R ₁ C ₅	98.0(3)
N ₂ -EC ₂	1.47(2)	Ni-S ₁ -R ₂ C ₆	97.6(3)
EC ₁ -EC ₂	1.58(2)	Ni-N ₁ -R ₁ C ₁	121.3(2)
EC ₁ -EM ₁	1.58(2)	Ni-N ₁ -EC ₁	116.1(3)
EC ₂ -EM ₂	1.58(3)	Ni-N ₂ -R ₂ C ₁	121.4(4)
N ₁ -R ₁ C ₁	1.36(2)	Ni-N ₂ -EC ₂	116.3(3)
N ₂ -R ₂ C ₁	1.37(2)	N ₁ -EC ₁ -EC ₂	107.7(3)
S ₁ -R ₁ C ₅	1.74(2)	N ₁ -EC ₁ -EM ₁	109.7(3)
S ₂ -R ₂ C ₆	1.68(2)	EC ₂ -EC ₁ -EM ₁	113.7(4)
R ₁ C ₁ -R ₁ C ₂	1.46(2)	N ₂ -EC ₂ -EC ₁	108.7(4)
R ₁ C ₂ -R ₁ C ₃	1.39(2)	N ₂ -EC ₂ -EM ₂	107.9(3)
R ₁ C ₃ -R ₁ C ₄	1.41(2)	EC ₁ -EC ₂ -EM ₂	112.9(4)
R ₁ C ₄ -R ₁ C ₅	1.42(2)	N ₁ -R ₁ C ₁ -R ₁ C ₆	114.9(4)
R ₁ C ₅ -R ₁ C ₆	1.40(1)	R ₁ C ₆ -R ₁ C ₁ -R ₁ C ₂	121.3(3)
R ₁ C ₆ -R ₁ C ₁	1.40(2)	R ₁ C ₁ -R ₁ C ₂ -R ₁ C ₃	116.3(3)
R ₂ C ₁ -R ₂ C ₂	1.46(2)	R ₁ C ₂ -R ₁ C ₃ -R ₁ C ₄	121.9(4)
R ₂ C ₂ -R ₂ C ₃	1.45(2)	R ₁ C ₃ -R ₁ C ₄ -R ₁ C ₅	121.4(2)
R ₂ C ₃ -R ₂ C ₄	1.36(2)	R ₁ C ₄ -R ₁ C ₅ -R ₁ C ₆	117.4(4)
R ₂ C ₄ -R ₂ C ₅	1.37(3)	R ₁ C ₅ -R ₁ C ₆ -R ₁ C ₁	121.3(3)
R ₂ C ₅ -R ₂ C ₆	1.45(2)	S ₁ -R ₁ C ₆ -R ₁ C ₁	115.6(3)
R ₂ C ₆ -R ₂ C ₁	1.39(3)	N ₂ -R ₂ C ₁ -R ₂ C ₆	114.6(3)
		R ₂ C ₆ -R ₂ C ₁ -R ₂ C ₂	122.6(3)
		R ₂ C ₁ -R ₂ C ₂ -R ₂ C ₃	118.7(3)
		R ₂ C ₂ -R ₂ C ₃ -R ₂ C ₄	125.6(2)
		R ₂ C ₃ -R ₂ C ₄ -R ₂ C ₅	119.8(3)
		R ₂ C ₄ -R ₂ C ₅ -R ₂ C ₆	120.0(4)
		R ₂ C ₅ -R ₂ C ₆ -R ₂ C ₁	119.1(3)
		S ₂ -R ₂ C ₆ -R ₂ C ₁	117.9(4)
Cation			
Av N-C	1.48(2)	Av N-C-C	110.2(4)
C-C	1.53(3)		

^a The labeling system used is illustrated in Figure 1. ^b Estimated standard deviation in the least significant figure is given in parentheses.

The structure reveals that the nickel atom is definitely four-coordinate and the inner NiN_2S_2 unit is planar. The equation of the best least-squares plane through the nickel, the two sulfur, and the two nitrogen atoms is $0.74x + 11.42y - 13.89z = 3.88$ (monoclinic coordinates). The deviations of the five atoms from this plane are: Ni, -0.022 (2); S₁, 0.023 (4); S₂, 0.016 (4); N₁, 0.10 (1); and N₂, 0.14 (1) Å. It should be noted, however, that the structural backbone of the anion (neglecting the methyl groups EM₁, EM₂) is only approximately planar. Both benzene rings are tilted out of the coordination plane in the same direction with the dihedral angle between the two planes determined by the atoms S₁, N₁, and R₁C₁, and S₂, N₂, and R₂C₁ being 168° . The nickel is located at a position which is slightly displaced from the line of intersection of these two planes. The distortion of the anion can be seen in Figure 1. The dihedral angles between the coordination plane and the planes determined by the benzene rings R₁ and R₂ are approximately 172° and 176° , respectively.

The equation of the best least-squares plane through the atoms Ni, S₁, S₂, N₁, N₂, EC₁, EC₂ is $1.71x + 11.40y - 13.92z = 3.88$ (monoclinic coordinates). The deviations of the seven atoms from this plane are given in Table IV. Inspection of Table IV reveals that the ethylene bridge has a puckered arrangement with respect to the coordination plane; carbon EC₁ is slightly above this plane and carbon EC₂ is slightly below it.

Table IV. Distances of Atoms from Best Plane through Ni, S₁, S₂, N₁, N₂, EC₁, and EC₂

Atom	Distance (Å) from plane
Ni	$-0.026(2)$
S ₁	$0.023(4)$
S ₂	$0.025(4)$
N ₁	$0.08(1)$
N ₂	$0.14(1)$
EC ₁	$0.11(1)$
EC ₂	$-0.06(1)$

The stereochemistry of the dimethyl-substituted ethylenediamine chelate ring is of particular interest. The two methyl groups EM₁ and EM₂ are significantly out of the plane determined by the atoms Ni, S₁, S₂, N₁, N₂, EC₁, and EC₂. The distances are 1.56 and 1.58 Å, for EM₁ and EM₂, respectively, with both methyl groups on the same side of this plane. In addition, we note that the average angles around carbon atoms EC₁ and EC₂ are 110.3 and 109.8° , respectively, which clearly indicates saturated carbon with resultant tetrahedral stereochemistry. Although the final difference Fourier is consistent with the saturated nature of the carbon atoms, the positions of both of the ethylene hydrogen atoms could not be located with absolute certainty. However, the stereochemistry of both carbon atoms in the ethylene bridge does provide a relatively unambiguous basis for the assignment of saturated carbon atoms in the bridge. Examination of the bond angles around the nitrogens N₁ and N₂ indicates that the nitrogens are trigonal planar and therefore they must not have any hydrogens attached to them. Furthermore, the bond lengths N₁-EC₁ and N₂-EC₂ are 1.50 and 1.47 Å, respectively, indicating single bonds. These distances can be compared with an N=C distance of 1.33 (4) Å as found in the structure of the biacetylbis(mercaptoethylimine)nickel(II) complex.¹¹ It is also of interest to note that the two C-N distances, R₁C₁-N₁ and R₂C₂-N₂, are 1.36 and 1.37 Å, respectively. These distances, which are crystallographically independent, establish significant double bond character in the two C-N bonds. In

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Table V. Summary of Esr, Optical Spectral, and Polarographic Data

Complex	$E_{1/2}$ for		g values			$\nu_{\max}, \text{cm}^{-1}$	
	$n = 0 \rightarrow n = -1$	$n = -1 \rightarrow n = -2$	$\langle g \rangle$	g_1	g_2		g_3
Ni(abt) ₂ ⁻	-0.720	-1.573	2.055 ^a	2.006	2.030	2.133 ^b	
Ni(gma)	-0.823	-1.605					10,350 (sh), 12,450 ^d
Ni(H ₂ gma) ⁻			2.051 ^a	2.009	2.027	2.119 ^b	10,200 (sh), 14,400, 16,900 ^e
Ni(dma)	-0.79	-1.58					10,400 (sh), 12,200 ^d
Ni(H ₂ dma) ⁻			2.050 ^a	2.007	2.028	2.121 ^b	10,300, 14,300, 16,950 ^e

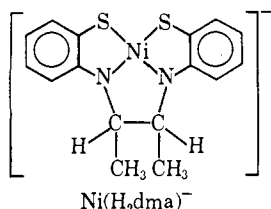
^a THF, CHCl₃. ^b Frozen DMF-CHCl₃ (1:1, v/v) at 77°K. ^c Potentials in volts measured in DMF using a dropping Hg electrode with Ag-AgClO₄ reference electrode. ^d Spectra in DMF. ^e Spectra in CH₂Cl₂.

conjunction with these bond lengths, we note that the two C-C distances $R_1C_1-R_1C_2$ and $R_2C_1-R_2C_2$ of 1.456 and 1.459 Å, respectively, are considerably longer than the C-C distances in a benzene ring. The possible significance of these bond lengths with respect to the electronic structure of the complex will be discussed later.

The tetraethylammonium cation appears normal with the expected tetrahedral stereochemistry around the nitrogen atom.

Discussion

The structural results leave little doubt that the green borohydride reduction product of Ni(dma) is in fact the bridge-saturated species Ni(H₂dma)⁻ shown below.

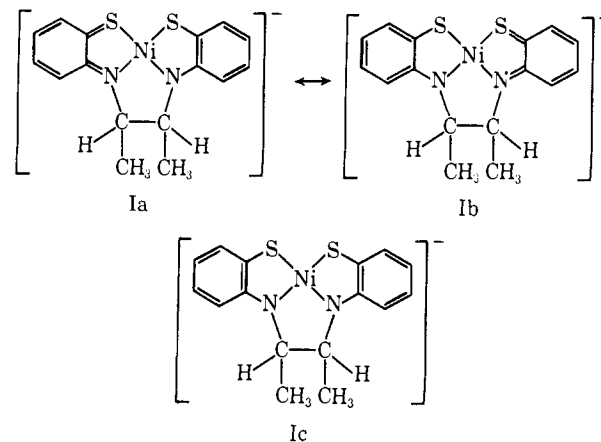


The exact mechanism by which the green paramagnetic species Ni(H₂dma)⁻ is obtained is not known, but since the experimental procedure calls for the presence of ethanol and air it is reasonable to suggest that it involves the dinegative ion Ni(H₂dma)²⁻. Esr, optical spectral, and polarographic data for Ni(abt)₂⁻, Ni(H₂dma)⁻, and Ni(gma)⁻ are summarized in Table V. The fact that Ni(H₂gma)⁻ and Ni(H₂dma)⁻ have essentially identical properties establishes an analogous bridge-saturated structure for the former complex.

Perhaps the most significant aspect of the structure of Ni(H₂dma)⁻ is the relatively short bond lengths between the benzene ring carbons, R_1C_1 and R_1C_2 , and N_1 and N_2 , respectively. Recent work has established that coordinated $C=N$ lies in the range of 1.29-1.34 Å, whereas coordinated $C-N$ is in the range of 1.44-1.51 Å.¹² In addition, the $C-NH_2$ distance in *p*-nitroaniline, where considerable double bond character is expected, is 1.37 Å.¹³ Thus, the two crystallographically independent distances $R_1C_1-N_1$ and $R_2C_1-N_2$, of 1.36 and 1.37 Å, respectively, convincingly demonstrate considerable double bond character in the two $C-N$ bonds, and point to contributions from resonance forms such as Ia and Ib. In fact, structures such as these taken at equal weight with a structure such as Ic would precisely predict the observed $C-N$ bond length. In addition, the lengths of the S-C bonds (1.74 for $S_2-R_1C_6$ and 1.69

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Å for $S_2-R_2C_6$) indicate multiple bond character between the sulfurs and the benzene rings as shown in resonance structures Ia and Ib. At this point it is noted that structures Ia and Ib are formally Ni(I) with the oxidized form of the ligand H_2dma^{2-} , whereas structure Ic is formally Ni(III) with the reduced form of the ligand H_2dma^{4-} . Thus, the four-coordinate, planar NiN_2S_2 structure is in good agreement with the coordinated radical formulation $[Ni(II)(H_2dma^{3-})]^-$, in which the ligand is partially oxidized and the metal has the d^8 configuration characteristic of planar coordination. It is difficult to reconcile the structural data with *either* a Ni(I) or a Ni(III) formulation.

Attention has already been called to the large difference in anisotropic g values between the coordinated radical anions Ni(H₂gma)⁻ and Ni(gma)⁻; specifically, there is much larger anisotropy in Ni(H₂gma)⁻. One explanation which has been given¹⁴ is that the unpaired electron in Ni(gma)⁻ is, to a very good approximation, isolated on the gma ligand, whereas in Ni(H₂gma)⁻ it sees much more of the metal d orbitals. While this seems reasonable at first glance, a more critical analysis of the esr data is desirable. The problem is that the anisotropy in the g tensor is in itself not a reliable criterion of metal d orbital involvement, particularly in complexes with ligands containing atoms with large spin-orbit coupling constants. Recently, the complex $Ni(Se_2C_2(CF_3)_2)_2$ ⁻¹⁵ has been prepared, and here the g tensor anisotropy is significantly greater than in the corresponding sulfur complex. It is probable that the symmetry of the orbital bearing the unpaired electron is the same in the two cases (which seems reasonable from gross similarities between the two complexes) and furthermore there are no significant differences in cova-

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lency. Thus, the greater g anisotropy observed for the $\text{Ni}(\text{Se}_2\text{C}_2(\text{CF}_3)_2)_2^-$ complex is interpreted simply as a consequence of the larger spin-orbit coupling in the selenium donor atoms. As additional support for this idea, we note that the low symmetry of the bound ligand requires three different components of the g tensor, and the heavy donor atoms may give a substantial magnitude to the anisotropy even in the absence of a metal contribution. A large anisotropy in the g tensor has been found for several arsine radical cations,¹⁶ and in sulfur containing radicals where g values as high as 2.056 have been observed.¹⁷ We must conclude that the greater g anisotropy exhibited by $\text{Ni}(\text{H}_2\text{gma})^-$ as compared to $\text{Ni}(\text{gma})^-$ does not necessarily mean that the unpaired electron in the former complex has substantially more metal character.

We offer the following interpretation for the dissimilarity in the esr spectra of $\text{Ni}(\text{H}_2\text{gma})^-$ and $\text{Ni}(\text{gma})^-$. From the fact that $\text{Ni}(\text{gma})^-$ has an intact α -diimine linkage which is known to participate widely in electron transfer reactions of the same type as those found for the dithiolene ligands,^{18,19} it follows that the α -diimine

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orbitals are probably of comparable energy to the metal d orbitals, and thus the precise composition and ordering of the molecular orbitals which contribute to the g values should be different for the two complexes in question. In addition, it is very possible that the unpaired electron in $\text{Ni}(\text{gma})^-$ actually resides in an orbital primarily delocalized over the α -diimine linkage. If this is the case, there is no reason to expect the g values for the two complexes to be the same.²⁰ We propose that it is only when the α -diimine bridge is chemically transformed by hydrogenation that the unpaired electron is forced to spend a large fraction of its time associated with the sulfur donor atoms. This proposal is consistent with the fact that the g tensor anisotropies in $\text{Ni}(\text{H}_2\text{gma})^-$ and $\text{Ni}(\text{abt})_2^-$ are virtually the same, and both are significantly larger than that observed for $\text{Ni}(\text{gma})^-$.

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Alkenylaryl Compounds of Nickel(II) and Palladium(II). Influence of the Transition Metal on Ligand Proton Chemical Shifts¹

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Abstract: Compounds of the type *trans*-chloro(2-allylphenyl)bis(triethylphosphine)metal(II) ($M = \text{Ni}, \text{Pd}$) and *trans*-X(2-vinylphenyl)bis(triethylphosphine)metal(II) ($M = \text{Ni}, X = \text{Cl}, \text{Br}, \text{I}, \text{NO}_2, \text{CN}, \text{NCS}, \text{NCO}$; and $M = \text{Pd}, X = \text{Br}$) have been synthesized and characterized. The pmr spectra of the compounds reveal that protons on the hydrocarbon ligands which are in close proximity to the metal exhibit low field shifts relative to chemical shifts of the corresponding protons in the parent hydrocarbons. An explanation of this phenomenon in terms of the paramagnetic anisotropy of the transition metal ion is presented.

Association of the weak temperature-independent paramagnetism exhibited by a number of transition metal complexes with a second order Zeeman effect is well established. Van Vleck³ proposed that transition metal ions possessing incompletely filled d levels, with all electrons paired in the ground state, may exhibit a weak paramagnetism in a magnetic field which derives from mixing of the ground state energy level with low-

lying excited states.⁴ The work of Van Vleck and coworkers served as a basis for the Ramsey theory which emphasizes the importance of a second order, paramagnetic contribution to the chemical shielding constant for a nucleus.⁵ The importance of this contribution to the shielding constant of a transition metal ion is best documented for $^{59}\text{Co}(\text{III})$ complexes.⁶ Thus, Proctor and Yu^{6a} first attributed the very large differences in the values of ^{59}Co chemical shielding constants for different cobalt complexes to temperature-inde-

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