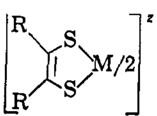
Electron-Transfer Complexes of the [M–N_2S_2] Type. The Existence of Cation-Stabilized Free-Radical Complexes

R. H. Holm,[1a] **A. L. Balch,**[1b] **A. Davison,**[2] **A. H. Maki,**[3a] **and T. E. Berry**[3a,b]

Contribution from the Departments of Chemistry, University of Wisconsin, Madison, Wisconsin, Massachusetts Institute of Technology, Cambridge, Massachusetts, and University of California, Riverside, California. *Received January 3, 1967*

Abstract: The propensity to undergo chemical and electrochemical one-electron-transfer reactions, already established in bis-chelate complexes of the general types [M–S_4]^z and [M–N_4]^z, has been shown to extend to two groups of [M–N_2S_2]^z complexes. The first group consists of bis-chelate species of presumed *trans* structure and is exemplified by bis(*o*-mercaptoanilido)nickel, Ni[*o*-C_6H_4(NH)S]$_2$, which undergoes two one-electron reductions in DMSO and dichloromethane solutions and one one-electron oxidation in dichloromethane solution. The mono anion ($z = -1$) of this four-member electron-transfer series has a doublet ground state and displays in glasses a markedly anisotropic g tensor, similar to those of [Ni–S_4]$^-$ and [Ni–N_4]$^-$ species, and, accordingly, is assigned a ^2B_g ground state with an appreciable admixture of metal orbital in the odd-electron wave function. The second group is composed of tetradentate complexes having a necessarily *cis*-N_2S_2 arrangement. Complexes of the types M(gma)^z, M(dtbh)^z, and Ni(dbh)^z were obtained with M = Ni, Cu, Zn, Cd (gma = glyoxalbis(*o*-mercaptoanil), dtbh = biacetylbis(thiobenzoylhydrazone), dbh = biacetylbis(benzoylhydrazone)). The Ni, Zn, and Cd neutral complexes are electrochemically reducible in nonaqueous media to $z = -1$ and -2 species. The monoanions possess doublet ground states. Their g tensors reveal a barely noticeable but unresolvable anisotropy (Ni) or no observable anisotropy (Zn, Cd). Because the Zn^- and Cd^- species can only be reasonably formulated as cation-stabilized free radicals (csfr), the properties of their g tensors are proposed as reasonable criteria for the appropriateness of csfr formulations, at least in [M–S_4]^z, [M–N_4]^z, and [M–N_2S_2]^z systems. The epr properties of the *cis*-[M–N_2S_2]^z complexes are interpreted in terms of a simple qualitative molecular orbital model, and probable ground states are assigned to five isoelectronic series of complexes of this general type.

The original demonstration[4] of the interrelationship of certain bis(*cis*-1,2-disubstituted ethylene-1,2-dithiolato) complexes (**1**) by electron-transfer reactions has been followed by extensive synthetic and physical investigations of these and related complexes.[5] Research in this area has taken two general directions. The first relates to the scope of electron-transfer reactions. It has been shown that neither an ethylenic ligand backbone nor an S_4 coordination sphere is a necessary condition for electron-transfer reactions because the complexes **2** (including ring-substituted variants)[6] and **3**, having X = Y = O,[7] X = Y = NH,[8] and X = O, Y = S,[9] undergo one or more such reactions. The presence of a five-membered delocalized chelate ring does appear to be required, however.[10]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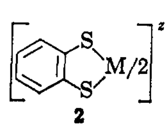
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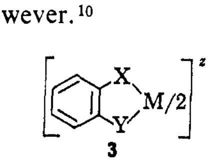
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The second research direction has been toward an elucidation of the ground- (and excited-) state descriptions of these complexes. Nearly all investigations have centered about the [$NiS_4C_4R_4$]$^-$ species, which have rich electronic spectra and doublet ground states. Their paramagnetic resonance spectra are readily observable in both fluid and glassy media, thereby permitting measurements of the isotropic g value and the principal components of the g tensor.

Among the essential features of any ground-state description in current molecular orbital theory are (i) specification of the symmetry of the highest occupied MO and, therewith, the possible metal and ligand orbitals admixed; and (ii) an estimate of the composition of this MO in terms of metal and ligand contributions. Of all nickel monoanions, Ni(mnt)$_2^-$ (**1**, R = CN) has been the most thoroughly studied.[11,12] Measurement of the spin-Hamiltonian parameters of this ion enriched in ^{61}Ni in an oriented, magnetically dilute, single crystal has led to the conclusion that the most probable ground-state configuration is $\ldots b_{3g}{}^1 b_{1g}{}^0$ and that the b_{3g} MO[13] has, very roughly, 50% metal character.[11,15] Application of semiempirical

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[1] University of Wisconsin: (a) Alfred P. Sloan Foundation Fellow; (b) National Science Foundation Predoctoral Fellow, 1963–1966.

[2] Massachusetts Institute of Technology.

[3] (a) University of California; (b) National Institutes of Health Predoctoral Fellow.

[4] A. Davison, N. Edelstein, R. H. Holm, and A. H. Maki, *J. Am. Chem. Soc.*, **85**, 2029 (1963).

[5] For one version of developments in this field through 1964, *cf.* H. B. Gray, *Transition Metal Chem.*, **1**, 239 (1965).

[6] (a) R. Williams, E. Billig, J. H. Waters, and H. B. Gray, *J. Am. Chem. Soc.*, **88**, 43 (1966); (b) M. J. Baker-Hawkes, E. Billig, and H. B. Gray, *ibid.*, **88**, 4870 (1966).

[7] F. Röhrscheid, A. L. Balch, and R. H. Holm, *Inorg. Chem.*, **5**, 1542 (1966).

[8] A. L. Balch and R. H. Holm, *J. Am. Chem. Soc.*, **88**, 5201 (1966).

[9] A. L. Balch, F. Röhrscheid, and R. H. Holm, *ibid.*, **87**, 2301 (1965).

[10] B. G. Werden, E. Billig, and H. B. Gray, *Inorg. Chem.*, **5**, 78 (1966); J. P. Fackler, Jr., and D. Coucouvanis, *J. Am. Chem. Soc.*, **88**, 3913 (1966).

[11] A. H. Maki, N. Edelstein, A. Davison, and R. H. Holm, *ibid.*, **86**, 4580 (1964).

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

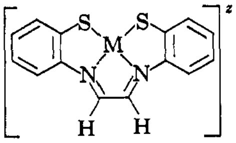
[13] Note that the defined x and y axes in D_{2h} symmetry are interchanged in ref 11 compared to ref 12 and 14; we refer to the axis system of ref 11 in which the origin is at the metal, the xy plane is that of the complex, and the y axis bisects the chelate rings. Thus the d_{yz} orbital has b_{3g} symmetry.

[14] G. N. Schrauzer and V. P. Mayweg, *J. Am. Chem. Soc.*, **87**, 3585 (1965).

[15] The most probable ground state was deduced by the best fit of the measured principal components of the g and A(^{61}Ni) tensors to theoretical expressions for these quantities calculated using perturbation theory and a basis set of pure metal 3d functions.[11] The use of this basis set has been criticized and the statement made that the epr results

MO theory has led to two different ground states for $[NiS_4C_4R_4]^-$. Shupack, *et al.*,[12] claim a $^2A_{1g}(\ldots a_{1g}b_{1g}^0)$ state and 26% metal character for the a_{1g} MO in $[Ni(mnt)_2]^-$. It is difficult to reconcile this ground state with the observed spin-Hamiltonian parameters.[11] Schrauzer and Mayweg[14] report calculations for the magnetically similar ion, $[NiS_4C_4H_4]^-$, leading to a likely $^2B_{3g}(\ldots b_{3g}{}^1b_{1g}{}^0)$ ground state and 18% metal character in the b_{3g} MO. Because spin-Hamiltonian parameters are the most demanding measurables of metal complexes to be reconciled with ground-state electronic properties, we feel that the description of $Ni(mnt)_2^-$ as containing, in a purely formal sense only, Ni(III) with the attendant d^7 configuration is not unreasonable and is the preferred formulation when interpreting epr properties.

Another formulation for $Ni(mnt)_2^-$, in conjunction with a $^2A_{1g}$ ground state, has been put forth.[12] This description involves Ni(II) with the odd electron delocalized on the ligands. Such a complex could be termed a cation-stabilized free radical (csfr). In strongly covalent complexes such as those considered here, any ground-state description in terms of a formal oxidation state of the metal (and, hence, of the ligands) or a csfr designation cannot be precise and must be an oversimplification, for both represent extreme cases. This point is well emphasized by $Ni(gma)^-$, the initial reduction product of glyoxalbis(*o*-mercaptoanil)nickel, Ni(gma)[17] (**4**, $z = 0$). Authentic $Ni(gma)^-$ [18] exhibits an observable but rather small *g*-tensor anisotropy[19] which renders either description inadequate. Obviously, what is needed is a complete MO description of the ground state for this and the other complexes considered. Because MO theory in its present semiempirical form cannot be considered reliable in predicting unique ground states for species of the complexity of **1–4**, we feel that it is useful to establish criteria for the application of the limiting descriptions. Accordingly, we report here our efforts to establish epr criteria for detectable involvement or lack of essential involvement of metal orbitals in the wave functions of unpaired electrons in complexes of the types **1–4**. As part of this work the electron-transfer properties of complexes of the type $[M\text{–}N_2S_2]$ have been investigated. The results augment those already obtained for $[M\text{–}S_4]$,[6] $[M\text{–}O_4]$,[7] $[M\text{–}N_4]$,[8] and $[M\text{–}O_2S_2]$[9] systems in which, principally, M = Ni. Certain of our results on gma complexes have been communicated in preliminary form.[19]



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Experimental Section

Preparation of Compounds. (a) Glyoxalbis(*o*-mercaptoanil) Complexes, $M(gma)^z$. Zn(gma) and Cd(gma) were prepared according to a published procedure.[17] Ni(gma) was obtained in an entirely analogous manner as shiny black crystals only sparingly soluble in most organic solvents. A freshly prepared sample was analyzed.

Anal. Calcd for $C_{14}H_{10}N_2S_2Ni$: C, 51.09; H, 3.06; N, 8.51; S, 19.49. Found: C, 51.20; H, 3.27; N, 8.22; S, 19.53.

$[(n\text{-}C_4H_9)_4N][Ni(gma)]$. The following operations were performed *in vacuo* or in a nitrogen atmosphere. A suspension of 3.6 g (0.012 mole) of Ni(gma) in 30 ml of dry, peroxide-free tetrahydrofuran was shaken with a dilute amalgam made from 0.23 g (0.010 g-atom) of sodium and 25 ml of mercury. A rapid reaction with heat evolution ensued to produce an intense red-brown solution, which was separated from the amalgam and filtered to remove unreacted, excess Ni(gma). The filtrate was treated with a solution of 3.5 g of tetra-*n*-butylammonium bromide in 300 ml of methanol. Agitation of the solution caused the product to separate as small needles during a 2–3-min period. It was collected by filtration and washed with methanol (three 20-ml portions). The product was dried at 25° (10^{-3} mm) for 10 hr and obtained as small, shiny, black crystals, soluble in polar organic solvents to give red-brown solutions. Oxidation of these solutions by air yields immediately Ni(gma).

Anal. Calcd for $C_{30}H_{14}N_3S_2Ni$: 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.

In this preparation it is important to note that a deficiency of sodium was used in the reduction. Excess sodium in the amalgam gives an emerald green solution, which is easily oxidized to a red-brown solution of $Ni(gma)^-$ and which presumably contains $Ni(gma)^{-2}$, whose existence is indicated by polarographic data (*cf.* Table I).

(b) Bis(*o*-mercaptoanilido)nickel. *o*-Mercaptoaniline (5.0 g) and 2.2 g of potassium hydroxide were dissolved in 100 ml of 20% aqueous ethanol. This solution was mixed with one prepared from 4.7 g of nickel chloride hexahydrate and 15 ml of concentrated aqueous ammonia in 75 ml of water. A yellow precipitate of bis(*o*-aminothiophenolato)nickel(II) formed immediately and was filtered off. The precipitate was suspended in 300 ml of water containing 4.0 g of potassium hydroxide; air was passed through the suspension for 5 hr. The deep blue solid which formed was collected by filtration, washed with water, and dried *in vacuo* over P_2O_5. The final product was obtained by two Soxhlet extractions with diethyl ether, which yielded deep blue crystals. A very similar procedure has been used by Hieber and Brück[20] to prepare a blue solid which they claimed to have the composition $[(C_6H_4(NH_2)S)]_4O_2Ni_2$.

Anal. Calcd for $C_{24}H_{24}N_4O_2S_4Ni_2$: C, 44.61; H, 3.75; N, 8.67; S, 19.85; Ni, 18.17. Calcd for $C_{12}H_{10}N_2S_2Ni$: C, 47.25; H, 3.30; N, 9.18; S, 21.02; Ni, 19.25. Found: C, 46.79; H, 3.71; N, 9.22; S, 21.02; Ni, 19.06 (total, 99.80).

(c) Biacetylbis(thiobenzoylhydrazone) Complexes [M(dtbh)]. The free ligand, H_2dtbh, and the nickel and copper complexes were obtained by the procedures of Bähr and Schleitzer.[21]

"must be reinterpreted in terms of a complete MO basis set"[16] on the grounds that the metal–ligand bonding is rather covalent[12] (*vide supra*). Implicit in this statement is the contention that *if* a complete basis set is used, a different ground-state description *might* emerge from the process of calculating *g* and *A* components using ***precalculated*** MO's of the ***entire*** complex. We suggest that it is unrealistic to assume that eigenvectors can be calculated so accurately by semiempirical procedures that their subsequent use, together with calculated or observed energy level separations, can generate *g* and *A* values of sufficient validity to permit a definitely more certain ground-state assignment than that made by use of a limited basis set. Covalency has been introduced in conjunction with the use of a limited basis set by reasonable reduction of free ion parameters in fitting measured parameters to theory.[11] The more usual use of epr data involves the evaluation of metal–ligand mixing coefficients from measured *g* and *A* values (*cf., e.g.*, A. H. Maki and B. R. McGarvey, *J. Chem. Phys.*, **29**, 31 (1958); H. R. Gersmann and J. D. Swalen, *ibid.*, **36**, 3221 (1962)) rather than the calculation of these values from preconstructed MO's of the complex. Finally, either procedure is a formidable task for molecular species of the complexity of 1, 2, or 3. In our previous work we have preferred to use the epr theory in a tractable form.

(16) E. I. Stiefel, J. H. Waters, E. Billig, and H. B. Gray, *J. Am. Chem. Soc.*, **87**, 3016 (1965).

(17) H. Jadamus, Q. Fernando, and H. Freiser, *ibid.*, **86**, 3056 (1964).

(18) Results already presented,[19] reinforced by more recent and thorough work (F. Lalor, M. F. Hawthorne, A. H. Maki, A. Davison, H. B. Gray, Z. Dori, and E. I. Stiefel, to be published), have convincingly demonstrated that the anion with a decidedly anisotropic *g* tensor which is produced by borohydride reduction of $Ni(gma)^0$ was incorrectly identified as $Ni(gma)^-$ in ref 16 and that the sodium amalgam reduction product (see Experimental Section) is actually $Ni(gma)^-$, as reported in ref 19.

(19) A. H. Maki, T. E. Berry, A. Davison, R. H. Holm, and A. L. Balch, *J. Am. Chem Soc.*, **88**, 1080 (1966).

(20) W. Hieber and R. Bruck, *Z. Anorg. Allgem. Chem.*, **269**, 13 (1952).

(21) G. Bahr and G. Schleitzer, *ibid.*, **280**, 161 (1955).

Table I. Polarographic Data for $[M-N_2S_2]^z$ and $[Ni-N_2O_2]^z$ Complexes

Complex	Couple $z \rightleftharpoons (z-1) + e^-$	Solvent	$E_{1/2}$, v[a]	i_d/C, μa/mmole
$Ni[o-C_6H_4(NH)S]_2^z$	$-2 \rightleftharpoons -1$	DMSO	−1.04	6.2
	$-1 \rightleftharpoons 0$	DMSO	−0.19	6.4
	$-2 \rightleftharpoons -1$	CH_2Cl_2	−0.93	22
	$-1 \rightleftharpoons 0$	CH_2Cl_2	−0.03	27
	$0 \rightleftharpoons +1$	CH_2Cl_2	1.05	27
$Ni[SC(C_6H_5)NNH]_2^z$	$-2 \rightleftharpoons -1$	DMSO	−1.13	6.4
	$-1 \rightleftharpoons 0$	DMSO	−0.14	6.6
$Ni(dbh)^z$	$-2 \rightleftharpoons -1$	DMSO	−1.67	5.8
	$-1 \rightleftharpoons 0$	DMSO	−0.92	6.1
		CH_3CN	−1.00	32
		CH_2Cl_2	−0.86	30
$Ni(dtbh)^z$	$-2 \rightleftharpoons -1$	DMSO	−1.24	6.9
		CH_3CN	−1.32	23
		CH_2Cl_2	−1.26	23
	$-1 \rightleftharpoons 0$	DMSO	−0.53	7.0
		CH_3CN	−0.55	33
		CH_2Cl_2	−0.48	28
$Cu(dtbh)^{z\,b}$	$-1 \rightleftharpoons 0$	DMSO	−0.15	6.3
		CH_3CN	−0.23	29
		CH_2Cl_2	−0.09	26
	$0 \rightleftharpoons +1$	CH_2Cl_2	1.15	25
$Zn(dtbh)^z$	$-2 \rightleftharpoons -1$	DMSO	−1.44	5.3
	$-1 \rightleftharpoons 0$	DMSO	−1.08	6.4
		CH_3CN	−1.10	25
		CH_2Cl_2	−1.31	23
$Cd(dtbh)^z$	$-2 \rightleftharpoons -1$	DMSO	−1.55	5.3
	$-1 \rightleftharpoons 0$	DMSO	−1.13	6.1
$Ni(gma)^z$	$-2 \rightleftharpoons -1$	DMSO	−1.05	6.9
	$-1 \rightleftharpoons 0$	DMSO	−0.30	6.5
$Zn(gma)^z$	$-2 \rightleftharpoons -1$	DMSO	−1.15	5.6
	$-1 \rightleftharpoons 0$	DMSO	−0.75	6.5
$Cd(gma)^z$	$-2 \rightleftharpoons -1$	DMSO	−1.33	5.2
	$-1 \rightleftharpoons 0$	DMSO	−0.79	6.5

[a] All potentials not strictly comparable; see Experimental Section. [b] Cu(dbh) shows poorly resolved wave in CH_2Cl_2 at ~ -0.49 v ($i_d/C \sim 19$)

Zn(dtbh). Biacetylbis(thiobenzoylhydrazone) (1.8 g) dissolved in 400 ml of ethanol was added to a solution of 1.1 g of zinc acetate dihydrate in 100 ml of ethanol. The solution volume was reduced to ~100 ml whereupon orange crystals separated. These were collected by filtration, recrystallized twice from 1:1 v/v chloroform–ethanol, and dried over P_2O_5 *in vacuo* at 80°. The purified product was isolated as reddish orange crystals.

Anal. Calcd for $C_{18}H_{16}N_4S_2Zn$: C, 51.74; H, 3.86; N, 13.41; S, 15.35. Found: C, 51.40; H, 3.99; N, 13.14; S, 15.05.

Cd(dtbh). A solution of 1.64 g of sodium acetate trihydrate and 3.44 g of cadmium bromide tetrahydrate in 60 ml of ethanol was prepared and filtered to remove sodium bromide. To this solution was added a boiling solution of 3.53 g of biacetylbis(thiobenzoylhydrazone) in 200 ml of ethanol. The resultant deep red precipitate was collected and washed with ethanol. Purification was effected by Soxhlet extraction with chloroform followed by drying at 80° *in vacuo*. A brick red microcrystalline product was obtained.

Anal. Calcd for $C_{18}H_{16}N_4S_2Cd$: C, 46.50; H, 3.47; N, 12.05. Found: C, 46.84; H, 3.44; N, 12.44.

(d) **Bis(thiobenzoylhydrazido)nickel.** A solution of 2.0 g (13 mmoles) of thiobenzoylhydrazine[22] in 100 ml of ethanol was added to a solution of 1.6 g (6.7 mmoles) of nickel chloride hexahydrate in 100 ml of ethanol. Addition of 80 ml of concentrated aqueous ammonia produced a beige precipitate. The mixture was stirred for 9 hr while air was passed through it. The resulting deep blue solid was collected by filtration, washed with ethanol, and vacuum dried; the yield of the crude product is 2.0 g (80%). One gram of this material was extracted with 150 ml of pure, dry tetrahydrofuran for 8 hr. Cooling of the solution afforded a deep blue, finely crystalline product which was collected and vacuum dried.

Anal. Calcd for $C_{14}H_{12}N_4S_2Ni$: C, 46.82; H, 3.37; N, 15.60; S, 17.86. Found: C, 46.79; H, 3.17; N, 15.41; S, 17.62.

(e) **Biacetylbis(benzoylhydrazone) Complexes, M(dbh).** The free ligand, H_2dbh, was prepared by dissolving 14.1 g (0.10 mole) of benzoylhydrazine and 4.4 g (0.05 mole) of biacetyl in 150 ml of 1-propanol, followed by refluxing for 6 hr. The solution was filtered when hot and the white microcrystalline product washed with ethanol and ether, mp 280–290° dec; lit.[23] 286°.

Ni(dbh). This compound was prepared according to Sacconi's method.[24]

Cu(dbh). A solution of 3.3 g of biacetylbis(benzoylhydrazone) and 0.8 g of sodium hydroxide in 70 ml of ethanol was added with stirring to a solution of 1.7 g of cupric chloride dihydrate in 50 ml of ethanol. The solution was allowed to stand for 1 hr after which brown crystals were isolated by filtration and dried. The crude product was twice recrystallized from 1:1 v/v chloroform–ethanol to yield greenish brown crystals which were dried over P_2O_5 *in vacuo* at 60°.

Anal. Calcd for $C_{18}H_{16}N_4O_2Cu$: C, 56.32; H, 4.20; N, 14.59. Found: C, 55.92; H, 4.31; N, 14.36.

Zn(dbh). This complex was prepared by the same procedure used for the cupric complex with the subsitution of zinc acetate for cupric chloride. The final product was obtained as fine yellow crystals.

Anal. Calcd for $C_{18}H_{16}N_4O_2Zn$: C, 56.05; H, 4.18; N, 14.53. Found: C, 55.42; H, 4.28; N, 14.01.

Physical Measurements. Polarographic data were obtained using an ORNL Model 1988 polarograph equipped with a three-electrode configuration. A rotating platinum electrode served as the working electrode. For measurements in acetonitrile and DMSO a saturated, aqueous calomel reference electrode and 0.05 *M* $(n-Pr_4N)ClO_4$ supporting electrolyte were employed. In dichloromethane solutions the supporting electrolyte was 0.1 *M* $(n-Bu_4N)(PF_6)$ and potentials were measured *vs.* a Ag–AgI reference electrode immersed in a 0.05 *M* $(n-Bu_4N)I$–0.5 *M* $(n-Bu_4N)PF_6$ solution in dichloromethane. The sample and reference compartments were connected by a salt bridge of silica gel impregnated with a dichloromethane solution of the supporting electrolyte. The entire arrangement for measurements in dichloromethane is described in detail elsewhere.[7] The potentials quoted in Table I were obtained from measurements of solutions prepared from the neutral complexes. Electron paramagnetic resonance measurements were made using a Varian V-4500 spectrometer with 100-kc/sec field modulation. The klystron frequency was measured by means of a transfer oscillator and frequency counter, and the magnetic field was measured with a proton resonance gaussmeter monitored by the same frequency counter.

Results and Discussion

Polarographic and epr results referred to in the following sections are set out in Tables I–III.

Electron-Transfer Properties of $[M-N_2S_2]$ Complexes. The possibility that complexes of this general type have electron-transfer properties was stimulated by the report of Hieber and Brück[20] that a deep blue product resulted from the reaction of bis(*o*-aminothiophenolato)nickel(II) with oxygen in basic solution. Earlier, Feigl and Fürth[25] had reported a very similar reaction of a nickel salt and *o*-phenylenediamine in aqueous ammoniacal solution which led to a deep blue product now known to have the formulation $Ni[o-C_6H_4(NH)_2]_2$ and to be the central member of a five-membered electron-transfer series.[8] An entirely analogous series, based on similar reasoning,[7,8] can be envisaged for the $[Ni-N_2S_2]$ system consisting of the members **5–9**. The Hieber–Brück product was claimed by them to have the composition $NiO[C_6H_4(NH_2)S]_2$ and the dimeric μ,μ-dioxo-bridged structure **10**; this formulation has been widely quoted in standard texts and references as one of the few Ni(IV) complexes. As communicated earlier,[9] repetition of this preparation[20] leads to a deep blue, diamagnetic compound whose *total* analysis corresponds to the composition $Ni[o-C_6H_4(NH)S]_2$.[26] That

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[22] B. Holmberg, *Arkiv Kemi*, **4**, 33 (1951).

[23] H. v. Pechmann and W. Bauer, *Ber.*, 42, 663 (1909).

[24] L. Sacconi, *Z. Anorg. Allgem. Chem.*, **275**, 249 (1954).

[25] F. Feigl and M. Fürth, *Monatsh.*, **48**, 445 (1927).

Table II. Epr Results for $[Ni\text{-}S_4]^-$ and $[Ni\text{-}N_4]^-$ Complexes[a]

Complex	Medium	$\langle g\rangle$	g_1	g_2	g_3	Ref
$[NiS_4C_4(CN)_4]^-$	DMF–$CHCl_3$	2.0633	1.996	2.043	2.140	4
	Single crystal[b]	(2.067)[c]	1.998	2.042	2.160	11
$[NiS_4C_4(CF_3)_4]^-$	DMF–$CHCl_3$	2.0618	1.996	2.044	2.137	*f*
$[NiS_4C_4(C_6H_5)_4]^-$	DMSO	2.056	...	...	...	4
$[NiS_4C_4H_4]^-$	py–$CHCl_3$	2.056[d]	1.996	2.039	2.126	14
$Ni(tdt)_2^-$	DMF–$CHCl_3$	2.082	2.016	2.048	2.183	6a
$Ni[o\text{-}C_6H_4(NH)_2]_2^-$	DMF–acetone	2.031[e]	1.990	2.006	2.102	8

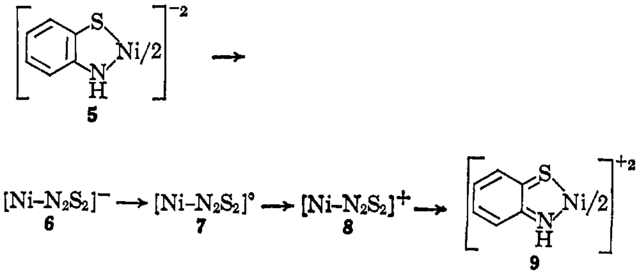
[a] $\langle g\rangle$ values are the measured values in solution unless otherwise stated; g_1, g_2, g_3 values obtained from glasses or single crystal. [b] Host crystal $(n\text{-}Bu_4N)[CuS_4C_4(CN)_4]$. [c] Calculated from anisotropic *g* values. [d] In pyridine solution. [e] 2.034 observed in DMSO solution.[16] [f] A. Davison, N. Edelstein, R. H. Holm, and A. H. Maki, *Inorg. Chem.*, **3**, 814 (1964).

Table III. Esr Results for $[M\text{-}N_2S_2]^z$ and $[M\text{-}N_2O_2]^z$ Complexes ($M = Ni, Cd, Zn, z = -1$; $M = Cu, z = 0$)

Initial Complex[a]	Medium[b]	Method of reduction[c]	$\langle g\rangle$ [d]	Glass, ~85°K. g_1	g_2	g_3
$Ni[o\text{-}C_6H_4(NH)S]_2$	2-MeTHF	Na(Hg)	2.0533	2.005	2.028	2.126
$Ni[SC(C_6H_5)NNH]_2$	2-MeTHF	Na(Hg)	2.0435	2.006	2.025	2.094
Ni(gma) (→Ni-$(H_2gma)^-$)[g]	DMF–$CHCl_3$	BH_4^-	2.051	2.009	2.027	2.119
Ni(gma)	DMSO–$CHCl_3$	cpe	(2.003)	1.978	2.005	2.026
	DMF	cpe	2.0041	...	...	...
	2-MeTHF	Na(Hg)	(2.004)	1.979	2.006	2.028
$(n\text{-}Bu_4N)[Ni(gma)]$	DMSO–$CHCl_3$	...	2.0041	1.980	2.004	2.025
	DMF–$CHCl_3$[f]	...	2.0042	1.975	2.005	2.026
Zn(gma)	DMF–$CHCl_3$	cpe			2.0027[h]	
	2-MeTHF	Na(Hg)			2.0033[h]	
Cd(gma)	2-MeTHF	Na(Hg)			2.0024[h]	
Ni(dbh)	CH_3CN	cpe	2.0006			
	2-MeTHF	Na(Hg)	2.0009		1.997[i]	
Ni(dtbh)	CH_3CN	cpe	1.9973			
	2-MeTHF	Na(Hg)	1.9979			
Cu(dbh)[j]	2-MeTHF	...	2.109	2.230 $(g_{\parallel})$	2.048 $(g_{\perp})$[e]	
Cu(dtbh)[k]	2-MeTHF, DMF–$CHCl_3$	...	2.062	...	...	
Zn(dtbh)	2-MeTHF	Na(Hg)	2.0023		2.0023	
Cd(dtbh)	2-MeTHF	Na(Hg)	2.0015		2.0015	

[a] Complex reduced (where appropriate) by method given in column 3. [b] Mixed solvents are 50–50 v/v. [c] cpe, controlled potential electrolysis; Na(Hg), 2% sodium amalgam. [d] Isotropic (solution) values; parentheses indicate value calculated from glass data. [e] Calculated from $\langle g\rangle$ and $g_{\parallel}$. [f] Fresh solution measured. [g] Reduction with borohydride in THF yields $Ni(H_2\text{-}gma)^-$, data from ref 18. [h] No measurable anisotropy in glass; spectra show additional line and half-field resonance compatible with triplet species. [i] Anisotropy not resolvable, measurement made at center of absorption. [j] $\langle a(^{63}Cu)\rangle = 7.19 \times 10^{-3}\ cm^{-1}$, $\langle a(^{14}N)\rangle = 1.13 \times 10^{-3}\ cm^{-1}$, $a_{\parallel}(^{63}Cu) = 1.68 \times 10^{-2}\ cm^{-1}$, $a_{\parallel}(^{14}N) = 1.37 \times 10^{-3}\ cm^{-1}$. [k] $\langle a(^{63}Cu)\rangle = 8.18 \times 10^{-3}\ cm^{-1}$, $\langle a(^{14}N)\rangle = 1.38 \times 10^{-3}\ cm^{-1}$.

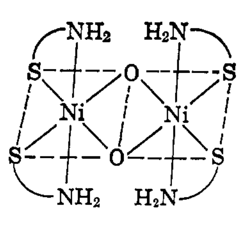
this compound is the central member **7** of the electron-transfer series **5–9** is evidenced by the two one-electron reductions in DMSO and a (very anodic) one-electron oxidation in dichloromethane. The most oxidized member, **9** has not been detected, probably because of the instability of the *o*-thionequinoneimine structure.



$$[Ni\text{-}N_2S_2]^- \longrightarrow [Ni\text{-}N_2S_2]^0 \longrightarrow [Ni\text{-}N_2S_2]^+ \longrightarrow$$

6 **7** **8**

Despite the relative ease with which the neutral complex is reduced to the monoanion by a variety of mild reducing agents, we have been as yet unable to isolate a pure salt of this species.



10

The electron-transfer propensity of Ni(gma) was first demonstrated by Stiefel, *et al.*,[16] who have shown that the series $Ni(gma)^z$ ($z = 0, -1, -2$) exists. The neutral nickel complex[17] as well as neutral complexes of other metals,[17,28] including zinc and cadmium,[17] have been isolated. We have verified the existence of the three-membered series in DMSO and DMF by polarography and have established by cyclic voltammetry the

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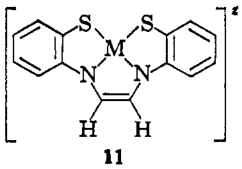
(26) The correct formulation of the Hieber–Brück product has also been recognized in reports[16,27] appearing shortly after our original communication.[9] Supporting evidence includes a parent ion peak in the mass spectrum at *m/e* 304[16] and the results of a total analysis including oxygen.[27]

(27) L. F. Larkworthy, J. M. Murphy, and D. J. Phillips, *J. Am. Chem. Soc.*, **88**, 1570 (1966).

(28) E. Bayer, *Angew. Chem.*, **73**, 659 (1961); **76**, 76 (1964).

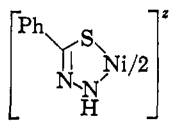
reversibility of the electrode reactions in DMF.[19] In addition, we have found that Zn(gma) and Cd(gma) in DMF and DMSO can be reduced in two reversible, one-electron steps to the mono- and dianions at potentials significantly more negative than those of the Ni(gma)^z system. Reduction of Ni(gma) with sodium amalgam in tetrahydrofuran has afforded the exceedingly oxygen-sensitive monoanion as the crystalline tetra-*n*-butylammonium salt. Because of their extreme oxidative instability, no attempt has been made to isolate the zinc or cadmium mono- and dianions or the nickel dianion.

An electron-transfer series analogous to **5**–**9** can be visualized for the M(gma)^z system. The terminal reduced member could be represented by **11** ($z = -2$) and the intermediate neutral member by **4** or **11** ($z = 0$) or some resonance combination thereof. The gma ligand system provides three five-membered chelate rings, each of which can be to some extent delocalized with concomitant change in formal oxidation state of the metal.[29] Obviously related delocalization possibilities exist in the neutral complexes of **1**, **2**, and **3**, thereby underscoring the electronic similarities of the ligand systems known to promote electron-transfer behavior.



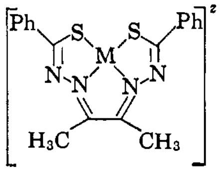
11

We have investigated the generality of electron-transfer reactions in other [M–N_2S_2] complexes by examining species having in principle delocalization properties analogous to those of **7** and **4** (or **11**) but with otherwise dissimilar ligand systems. In this connection we have reexamined the work of Jensen and Miguel,[30] who have reported that a deep blue product of apparent composition Ni[SC(Ph)NNH]$_2$ results from the aerobic oxidation of an ammoniacal solution of nickel chloride and thiobenzoylhydrazine. We have obtained this product under similar conditions and confirmed its composition. The oxidation presumably proceeds through the intermediates Ni[SC(Ph)NHNH$_2$]$_2$Cl$_2$ and Ni[SC(Ph)NHNH]$_2$, both of which have been isolated.[30] The deep blue product can be reduced polarographically in DMSO to the $z = -1$ and -2 species at potentials very similar to those of the Ni[o-C$_6$H$_4$(NH)S]$_2^z$ system. The structures of the Ni[SC(Ph)NNH]$_2^z$ species can be represented by **12** and other appropriate valence-bond representations.[31]



12

Biacetylbis(thiobenzoylhydrazone) complexes, one representation of which is **13**,[32] bear the same resemblance to Ni[SC(Ph)NNH]^z as does M(gma)$_1^z$ to Ni-[o-C$_6$H$_4$(NH)S]$_2^z$. Accordingly, these complexes, first prepared by Bähr and Schleitzer,[21] do undergo electron-transfer reactions. The neutral complexes with M = Ni, Zn, Cd may be reduced in two one-electron steps to the $z = -1$ and -2 species in DMSO. Because of the apparent instability of Ni(gma)$^-$ in at least one solvent medium,[18,19] we have verified the existence of the $-1 \rightleftarrows 0$ couple of nickel–, copper–, and zinc–dtbh complexes in three solvents. The M(dtbh)$^-$ species are considerably more oxidatively unstable than are the corresponding M(gma)$^-$ complexes, and isolation of them has not proven feasible. Cu(dtbh) is particularly easily reduced to a monoanion, but despite a number of attempts we have not been able to isolate a pure salt of this ion.



13

Several complexes of biacetylbis(benzoylhydrazone) have been prepared. These differ from **13** only in having oxygen in place of sulfur. Ni(dbh) undergoes two one-electron reductions in DMSO where it presumably exists as a paramagnetic, solvated species. Only the first reduction is observed in dichloromethane and acetonitrile, in which the neutral complex is diamagnetic and occurs at potentials significantly more negative than those for Ni(dtbh) in the same solvents. Cu(dbh) and Zn(dbh) do not undergo well-defined one-electron reductions.

Epr Results. (1) [Ni–S$_4$]$^-$ and [Ni–N$_4$]$^-$ Complexes. A collection of g-value data for all presently known anions of these types is given in Table II. It is evident that all complexes are markedly anisotropic and that isotropic and anisotropic g values of [NiS$_4$C$_4$R$_4$]$^-$ species are virtually independent of R. It is concluded that all of these ions, including Ni[o-C$_6$H$_4$(NH)$_2$]$_2^-$, very probably have the same ground state although the extent of electron delocalization may differ somewhat among the species. On the basis of previous work[11] the probable ground state is $^2B_{3g}$, which generates the following characteristic features in these anions:[33] (i) $\langle g \rangle$ equal to or in excess of 2.03 and a lower limit of $\sim$2.05 for [Ni–S$_4$]$^-$; (ii) three observable principal g values, showing that the effective ligand field is of rhombic, not axial, symmetry. These observations do not support a pure csfr description of the ground state. Although three principal g values have been observed

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(29) No X-ray structural information on gma complexes is available so that the relative contributions of 4 and 11 to the ground state of neutral complexes is unknown. The structure of the related complex biacetylbis(mercaptoethylimine)nickel has been reported (Q. Fernando and P. J. Wheatley, *Inorg. Chem.*, 5, 1726 (1966)); this species could in principle be considered the neutral parent of a three-membered electron-transfer series with $z = 0, -1, -2$. The large standard deviations of reported distances in the C$_2$N$_2$ chelate ring, common to this species and M(gma), preclude conclusions relative to delocalization in this ring.

(30) K. A. Jensen and J. F. Miguel, *Acta Chem. Scand.*, 6, 189 (1952).

(31) Note that valence bond structures can be written for Ni[o-C$_6$H$_4$(NH)S]$_2^0$ and Ni[SC(Ph)NNH]$_2^0$ which are entirely analogous to those for [NiS$_4$C$_4$R$_4$]^0 (*cf.* ref 14).

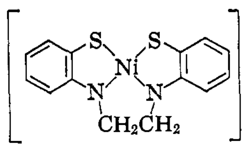
(32) The structure of the related complex, 2-keto-3-ethoxybutyraldehydebis(thiosemicarbazone)copper has been briefly reported (M. R. Taylor, E. J. Gabe, J. P. Glusker, J. A. Minkin, and A. L. Patterson, *J. Am. Chem. Soc.*, 88, 1845 (1966)). The complex is planar and is depicted as having an α-diimine chelate ring; bond angles and distances were not given.

(33) An analogous ground state (^2B_g in C_{2h} symmetry) applies for Ni[o-C$_6$H$_4$OS]$_2^-$ which has $\langle g \rangle = 2.083$, $g_1 = 2.017$, $g_2 = 2.036$, $g_3 = 2.191$ (DMF–CHCl$_3$),[9] values nearly identical with those of Ni(tdt)$_2^-$ in the same medium.[6a]

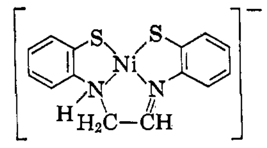
in frozen solutions of sulfur and sulfur-containing radicals[34] and in irradiated single crystals of sulfur-containing compounds,[35] the largest anisotropic value observed is 2.066.[36] Furthermore, in radicals where it is highly probable that the odd electron is essentially localized on the sulfur atom, $\langle g \rangle$ has not been observed to exceed 2.03[34] and is frequently ~2.01. For example, in the radical anion of 1,8-naphthalene disulfide, $\langle g \rangle = 2.0110$; extended Hückel calculations predict nearly complete localization of the odd electron on the sulfur atoms.[37] Likewise, in the species which is apparently the 2,4,6-tri-*t*-butylphenylmercapto radical, ^{33}S hyperfine splitting and $\langle g \rangle = 2.0104$ are found.[38] We conclude that the larger *g*-value anisotropies and isotropic *g* values of the complexes in Table II are manifestations of appreciable admixture of d orbitals of the metal in the wave function of the odd electron. As already remarked, the anisotropic and isotropic *g* values of $Ni(mnt)_2^-$, as well as the ^{61}Ni hyperfine splitting tensor, can be quantitatively accounted for by a $^2B_{3g}$ ground state and a relatively large degree of metal–ligand covalent bonding.

(2) Bis-Bidentate $[M-N_2S_2]^z$ Complexes. $Ni[o\text{-}C_6H_4(NH)S]_2^-$ and $Ni[SC(C_6H_5)NNH]_2^-$ were prepared by sodium amalgam reduction in 2-methyltetrahydrofuran solution but were not isolated. Both ions give convincingly similar epr spectra with the general features i and ii above. Hyperfine splitting was not observed in solution. Because of the close relationship between the *g* values of these complexes and those in Table II, it is concluded that a ^2B_g ground state (assumed C_{2h} symmetry) is very probable for these $[Ni-N_2S_2]^-$ species.[39]

(3) M(gma)$^-$ Complexes. Ni(gma) has been reduced by controlled potential electrolysis in DMSO–$CHCl_3$ solution and by treatment with sodium amalgam in 2-methyltetrahydrofuran. Both methods generate species with *g* values only slightly above the free-electron value (2.0023) and with a *g* anisotropy markedly less than those of bis-bidentate $[M-N_2S_2]^-$ or $[M-S_4]^-$ complexes. Further, the analyzed salt (n-Bu_4N)[Ni(gma)] in DMSO–$CHCl_3$ solution or in a *freshly prepared* DMF–$CHCl_3$ solution gives isotropic and anisotropic *g* values within experimental error of those obtained by electrochemical or chemical reduction of Ni(gma). Previously, borohydride reduction of Ni(gma) was thought to produce Ni(gma)$^-$.[16] This is now known not to be the case and the product obtained has been identified as the bridge-hydrogenated species **14a** or **14b**,[18] $Ni(H_2gma)^-$. The borohyride reduction product is reported[16] to have $\langle g \rangle = 2.051$, $g_1 = 2.009$, $g_2 = 2.027$, $g_3 = 2.119$, values very similar to those of the bisbidentate $[Ni-N_2S_2]^-$ species.



14a



14b

Two particular advantages of the gma system over the bidentate ligands in **1**–**3** are that the zinc and cadmium complexes, if monomeric, are constrained to have a more or less planar structure similar to that which Ni(gma) (diamagnetic) surely possesses, and that they are reducible to monoanions.[40] Zn(gma)$^-$ and Cd(gma)$^-$ can only be reasonably formulated to contain Zn(II) and Cd(II) with closed-shell d^{10} configurations and a coordinated radical-anion ligand and, therefore, should be useful for establishing criteria of metal orbital involvement in the odd-electron wave functions of $[M-N_2S_2]$ complexes. The *g* tensors of Zn(gma)$^-$ and Cd(gma)$^-$ are isotropic in glasses to the limit of resolution and have values extremely close to that of a free spin.

(4) M(dtbh)$^{0,-1}$ Complexes. Sodium amalgam reduction of Zn(dtbh) and Cd(dtbh) affords the monoanions whose *g* values are virtually identical with those of the corresponding gma species. Values very near the free-electron value are found and no anisotropy is measurable in glasses of 2-methyltetrahydrofuran. Ni(dtbh)$^-$ prepared by chemical or electrochemical reduction exhibits isotropic *g* values just under the free-electron value and a barely noticeable anisotropy in 2-methyltetrahydrofuran glass which was, however, not sufficiently well resolved to measure. It is apparent that the degree of metal orbital involvement in Ni(dtbh)$^-$ is scarcely detectable by epr measurements and is only slightly greater than that of Zn(dtbh)$^-$ and Cd(dtbh)$^-$, which is not detectable. Cu(dtbh)^0 solutions in 2-methyltetrahydrofuran and DMF–$CHCl_3$ give at room temperature a spectrum characteristic of planar Cu(II) complexes.[43] Hyperfine splittings due to $^{63,65}Cu$ and ^{14}N are clearly resolved. The spectrum in frozen glasses (~85°) is complex and has not been fully interpreted as yet.

(5) M(dbh)$^{0,-1}$ Complexes. Generation of Ni(dbh)$^-$ was accomplished by chemical or electrochemical reduction of the neutral complex. The epr properties of this anion are nearly identical with those of Ni(dtbh)$^-$, *viz.*, an isotropic *g* value very near the free-electron value and a barely observable anisotropy in 2-methyltetrahydrofuran glass which is too small to measure. The epr spectrum of Cu(dbh) is entirely usual for a Cu(II) complex with an O_2N_2 coordination sphere.[43]

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(34) W. G. Hodgson, S. A. Buckler, and G. Peters, *J. Am. Chem. Soc.*, **85**, 543 (1963); J. J. Windle, A. K. Wiersema, and A. L. Tappel, *J. Chem. Phys.*, **41**, 1996 (1964); A. Zweig and W. G. Hodgson, *Proc. Chem. Soc.*, 417 (1964); and references therein.

(35) K. Akasaka, *J. Chem. Phys.*, **45**, 90 (1966), and references therein.

(36) An exception to this statement is found with the radical obtained by electron bombardment of a single crystal of L-cysteine hydrochloride, which has $g_x = g_y = 1.99$, $g_z = 2.29$: K. Akasaka, *ibid.*, 43, 1182 (1965). The large value of g_z is attributed to a near-degeneracy of the $3p_x$ and $3p_y$ sulfur orbitals, one of which is occupied by the odd electron. A similar situation should not be present in the complexes under discussion.

(37) A. Zweig and A. K. Hoffman, *J. Org. Chem.*, **30**, 3997 (1965).

(38) W. Rundel and K. Scheffler, *Angew. Chem.*, **77**, 220 (1965).

(39) In D_{2h} symmetry any of the ground states (^2A_g, $^2B_{2g}$, $^2B_{3g}$) considered in our previous analysis does in principle require a threefold antisotropy of the *g* tensor.[11] Our designation of the ^2B_g ground state as most probable for these $[Ni-N_2S_2]^-$ complexes is based only upon the anisotropies of their *g* tensors, which are about the same as those of the $[Ni-S_4]^-$ species.

(40) The only zinc complexes of the type $[Zn-S_4]^z$ which have been reported are $Zn(tdt)_2^{-2}$ [41] and $Zn(mnt)_2^{-2}$.[42] No analogous cadmium complexes are known nor are any $[M-N_4]^z$ species of either metal. Unlike other $M(mnt)_2^{-2}$ complexes, $Zn(mnt)_2^{-2}$ is very probably tetrahedral,[42] and in acetonitrile or dichloromethane it does not undergo a discrete one-electron oxidation.

(41) W. H. Mills and R. E. D. Clark, *J. Chem. Soc.*, 175 (1936).

(42) E. Billig, R. Williams, I. Bernal, J. H. Waters, and H. B. Gray, *Inorg. Chem.*, **3**, 663 (1964).

(43) A. H. Maki and B. R. McGarvey, *J. Chem. Phys.*, **29**, 31, 35 (1958); D. Kivelson and R. Neiman, *ibid.*, **35**, 149 (1961); A. K. Wiersema and J. J. Windle, *J. Phys. Chem.*, **68**, 2316 (1964).

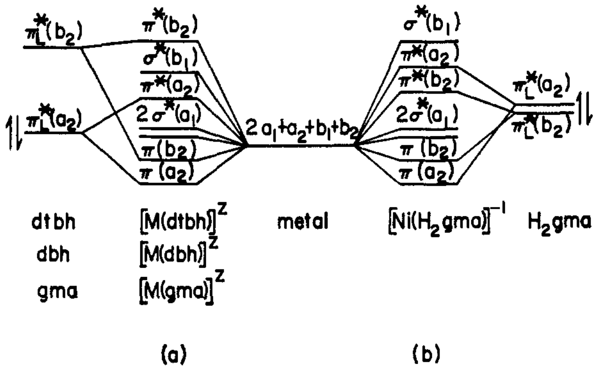


Figure 1. Qualitative molecular orbital diagrams for *cis*-$[M–S_2N_2]^z$ complexes: (a) $[M(dtbh)]^z$, $[M(dbh)]^z$, $[M(gma)]^z$ complexes (see text for comments about variable energy order of $\sigma^*(b_1)$ and $\pi^*(b_2)$); (b) *sym*-$Ni(H_2gma)^-$.

Criteria of Metal-Orbital Involvement. We take as models for the paramagnetic dtbh and gma complexes in which there will be minimal metal orbital involvement in the odd-electron wave functions the monoanions of zinc and cadmium. In the neutral complexes both the ligand and metal have closed-shell configurations. The odd electron added in the first reduction step is then described by what must be an essentially ligand-based MO (*vide infra*). The *g* tensors anticipated approach those of an aromatic free radical. The extent to which sulfur atoms will increase the *g* value above the free-electron value by spin–orbit coupling is difficult to predict. On the basis of available results this effect is slight in aromatic radicals.[44] Accordingly, it is proposed that gma and dtbh complexes having coordinated radical-anion ligands should manifest the following *g*-tensor properties characteristic of aromatic radicals:[45] (i) isotropic values less than ~2.01, and (ii) slight or unresolvable anisotropy. As pointed out elsewhere,[18] when comparing complexes of the same metal with different ligands, it is especially desirable to have measurement of the anisotropic dipole–dipole contribution to the electron–nucleus hyperfine tensor in addition to the principal components of the *g* tensor. However, such information is available only for $Ni(mnt)_2^-$ so conclusions about metal-orbital involvement can be drawn only from properties of the *g* tensors.

Using these criteria the paramagnetic complexes considered in this work are assigned the ground-state descriptions as shown in Table IV. The classification of $Ni(gma)^-$ is perhaps least satisfactory. Compared to the $[Ni–S_4]^-$ and the $[Ni–N_4]^-$ species, this complex has the least metal admixture in the odd-electron orbital, as judged from the smaller *g* anisotropy, such that this orbital is mostly, *but not completely*, ligand-based.

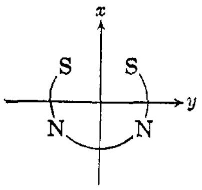
The most striking correlation which is apparent in the classification of the $[Ni–S_2N_2]^-$ complexes is the effect of bridge conjugation on the description of the ground state. This effect is well illustrated by the comparison of $Ni(H_2gma)^-$ and $Ni(gma)^-$, where the *cis* geometry is maintained. Conjugation of the ligands leads to a striking reduction in the *g* tensor (*cf.* Table III), consistent with an increase in the ligand character of the half-filled molecular orbital. This correlation has prompted us to deduce from the paramagnetic resonance results a qualitative molecular orbital model for bonding in these complexes.

Table IV

$^2B_{3g}$ or ^2B_g with appreciable metal-orbital admixture	Csfr, Ni(II), d^8	Cu(II), d^9	Csfr, M(II), d^{10}
$[NiS_4C_4R_4]^-$	$Ni(gma)^-$	Cu(dbh)	$Zn(gma)^-$
$Ni(tdt)_2^-$	$Ni(dbh)^-$	Cu(dtbh)	$Zn(dtbh)^-$
Ni[*o*-$C_6H_4(NH)_2]_2^-$	$Ni(dtbh)^-$		$Cd(gma)^-$
Ni[*o*-$C_6H_4(NH)S]_2^-$ [a]			$Cd(dtbh)^-$
$Ni[SC(Ph)NNH]_2^-$ [a]			
$Ni(H_2gma)^-$ [b]			

[a] Assumed *trans* (C_{2h}) structure. [b] Possible ground states: $^2A_2$-(C_{2v}, **14a**), ^2A(C_1, **14b**).

Simplified Bonding Model. *cis*-$[M–N_2S_2]^z$ complexes possess the common chelate ring structure (**15**) of C_{2v} symmetry. The π and σ MO's transform as $a_2 + b_2$ and $a_1 + b_1$, respectively. Symmetries of the metal orbitals are as follows: a_1 – d_{z^2}, $d_{x^2-y^2}$, s, p_x; a_2 – d_{yz}; b_1 – d_{xy}, p_y; b_2 – d_{xz}, p_z. Because of the over-all complexity of these systems, we outline what appears to be the simplest possible model. A partial, qualitative MO diagram for $[M(dtbh)]^z$, $[M(dbh)]^z$, and $[M(gma)]^z$ complexes is set out in Figure 1a. The orbitals shown are those which presumably will have significant metal character and/or those which will be relevant in ground-state descriptions. The complex metal–ligand orbital mixing allowed by symmetry has been simplified by assuming that, for the purpose of ground-state descriptions, the most important π mixing will involve ligand orbitals which are most nearly nonbonding; these are just those which are the highest filled and lowest vacant orbitals in the dinegative ligand. The energy order, symmetries, and eigenvectors of these orbitals were obtained from a series of Hückel calculations.[46] The results are given in Table V. The coefficients c_6–c_{10} (not shown) are obtained for the a_2 and b_2 orbitals by multiplying c_1–c_5 by -1 and $+1$, respectively. For dtbh, dbh, and gma, the forms of $\pi^*(a_2)$



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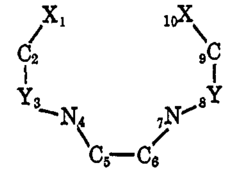
[44] It is significant to note that $\langle g \rangle = 2.03$ and $\Delta g_{max} = 0.06$ have thus far been observed only in alkylsulfur radicals, where substantial delocalization of the odd spin onto the hydrocarbon portion is unlikely.

[45] For a tabulation and discussion of *g* tensors of oriented π-electron free radicals (not containing sulfur), *cf.* J. R. Morton, *Chem. Rev.*, **64**, 453 (1964).

(46) To assure the reliability of the energy orders and general forms of the eigenvectors, the ordinary Hückel parameters *k* and *h* in $\alpha_i = \alpha + h_i\beta$ and $\beta_{ij} = k_{ij}\beta$ were varied over wide ranges in calculations for gma, dtbh, and dbh. Particular attention was given to the sulfur parameters whose suggested values are variant and dependent on the specific system and property under investigation.[47] Representative results were obtained with $\beta_{CN} = \beta_{NN} = \beta$ and $\alpha_N = \alpha + 0.5\beta$ for the three ligands. Using these parameters and simultaneously varying k_{CS} and h_S over the limits $0.5 \leq k_{CS} \leq 1.5$ and $0 \leq h_S \leq 2$, it is found that for dtbh and gma the energy differences between $\pi^*(a_2)$ and $\pi^*(b_2)$, $\pi^*(a_2)$ and the next most stable MO, and $\pi^*(b_2)$ and the next highest MO are all ~0.4–0.8β or more.

(47) D. S. Sappenfield and M. M. Kreevoy, *Tetrahedron Suppl.*, **2**, 157 (1963); A. Kuboyama, *J. Am. Chem. Soc.*, **86**, 164 (1964); R. Gerdil and E. A. C. Lucken, *ibid.*, **87**, 213 (1965); E. T. Strom and G. A. Russell, *ibid.*, **87**, 3326 (1965). For a discussion of sulfur parameters in HMO theory, *cf.* R. Zahradnik, *Advan. Heterocyclic Chem.*, **5**, 1 (1965).

Table V. Molecular Orbitals of dtbh, dbh, gma, and H_2gma[a]

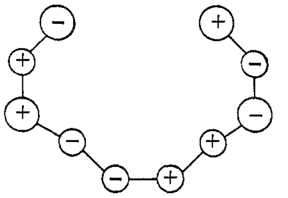


dtbh: X=S, Y=N
dbh: X=O, Y=N
gma, H_2gma: X=S, Y=C

	MO	$E(\beta)$	c_1	c_2	c_3	c_4	c_5
dtbh[b,c]	$\pi_L^*(a_2)$	0.1031	−0.3697	+0.1467	+0.3962	−0.3040	−0.2755
	$\pi_L^*(b_2)$	−0.4236	−0.3159	+0.2918	+0,0811	−0.3667	+0.2576
dbh[c,d]	$\pi_L^*(a_2)$	0.1659	−0.2316	+0.2059	+0.4078	−0.3422	−0.2935
	$\pi_L^*(b_2)$	−0.4397	−0.2327	+0.3010	+0.0958	−0.3910	+0.2716
gma[b]	$\pi_L^*(a_2)$	0.1504	−0.4518	+0.1579	+0.2538	−0.2082	−0.1810
	$\pi_L^*(b_2)$	−0.2998	−0.2170	+0.1736	+0.0128	−0.4224	+0.3250
sym-H_2gma[b]	$\pi_L^*(b_2)$ $\pi_L^*(a_2)$	0.0000	−0.5345	+0.2673	+0.2672	−0.5345	. . .

[a] All results obtained with $\beta_{CN} = \beta_{NN} = \beta, \alpha_N = \alpha + 0.5\beta$. [b] $\beta_{CS} = \beta_{CN} = \beta, \alpha_S = \alpha + 0.5\beta$. [c] $\beta_{NN} = \beta$, phenyl groups coplanar with rest of molecule. [d] $\alpha_O = \alpha + 1.5\beta$.

(**16**) and $\pi^*(b_2)$ (**17**) are shown below in schematic form. On the basis of the form of its eigenvector $\pi^*(a_2)$



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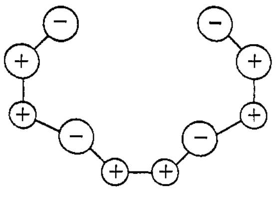

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is expected to mix significantly with d_{yz}. On the other hand, *overlap of π_2^* (b_2) with d_{xz} is not large, and presumably little mixing occurs. On this basis $\pi^*(b_2)$ in Figure 1a is heavily ligand in character.*

The tetradentate complexes which have been isolated or generated chemically or electrochemically in solution fall into the isoelectronic groups I–V below, arranged in order of increasing number of valence electrons. The dtbh system offers the broadest base for ground-state comparisons because all species in these groups have been prepared or generated. In addition to the epr data already discussed, it is noted that Ni^0, Zn^0, and Cd^0 complexes are diamagnetic. No direct evidence is available relating to the ground states of Cu^+ in group I, Ni^{-2} or Cu^- in group III, and Zn^{-2} and Cd^{-2} in group V. Examining first group II complexes, the epr data leave little doubt that the ground states of Cu^0 and Ni^- are different. Both Cu(dbh) and Cu(dtbh) give characteristic spectra of Cu(II) complexes having near-axial symmetry. Referring to Figure 1a, these complexes are assigned the configuration...$\sigma^{*1}(b_1)$. $Ni(dtbh)^-$ and $Ni(dbh)^-$, on the other hand, manifest spectra not compatible with this configuration. Their csfr formulations are best accommodated by inverting the order of $\sigma^*(b_1)$ and $\pi^*(b_2)$, leading to the configuration ... $\pi^{*1}(b_2)$. A slight admixture of d_{xz} in this MO and/or mixing in other configurations by spin–orbit coupling could account for the just noticeable but unresolvable g-tensor anisotropy. All MO's in group I complexes up to and including $\pi^*(a_2)$ are filled. The configuration of the Ni^0 complexes is presumably ... $\pi^2(b_2)$, $2\sigma^{*4}(a_1)$, $\pi^{*2}(a_2)$. The relative order of these orbitals is not known, but the results on group II complexes strongly indicate that they are of lower energy than $\sigma^*(b_1)$ or $\pi^*(b_2)$. In group III the ...$\sigma^{*2}(b_1)$ configuration for Zn^0 and Cd^0 is assigned. The possibility of triplet ground states, *viz.*, $\sigma^{*1}(b_1)$ $\pi^{*1}(b_2)$, for Cu^- and Ni^{-2} is recognized, but no information is available. The $\pi^{*1}(b_2)$ configuration is believed to apply to the group IV species. Here metal orbital admixture, as reflected by the epr results, is minimal due to the stability of the effective d^{10} configuration of the coordinated metal. The $\pi^{*2}(b_2)$ configuration follows for the species of group V.

I	II	III	IV	V
Ni^0	Ni^-	Ni^{-2}		
Cu^+	Cu^0	Cu^-		
		Zn^0	Zn^-	Zn^{-2}
		Cd^0	Cd^-	Cd^{-2}

Finally, attention is turned to a comparison of $Ni(gma)^-$ and $Ni(H_2gma)^-$, which have markedly different g tensors. For H_2gma in both the symmetrical (**14a**, *sym*) and unsymmetrical forms (**14b**, *unsym*), a series of Hückel calculations similar to those for gma was performed[46] but with $\beta_{CC} = 0$ and one or both β_{CN} values for the bridge taken as zero. Compared to gma, the absence of a conjugated bridge π system in either structure leads, in any calculation, to a much reduced interaction of the two halves of the ligand system. It is just this effect which is believed to account for the difference in magnetic properties of the two complexes. Because the detailed structure of $Ni(H_2gma)^-$ is at present unknown, **14a** is selected as the model structure for investigating the effect of bridge hydrogenation on ground-state electronic properties. Use of this structure facilitates a direct comparison with the parent ion, $Ni(gma)^-$, for both have idealized C_{2v} symmetry. In *sym*-H_2gma^{-2} the ligand orbitals taken to be most important in π mixing with the metal orbitals are $\pi_L^*(b_2)$ and $\pi_L^*(a_2)$, both of which have a Hückel energy of 0β.[48] These orbitals have forms similar to **16** and **17** but with no contribution from the bridge carbon atoms (*cf.* Table V). As before, $\pi_L^*(a_2)$ will mix much more strongly with d_{yz} than will $\pi_L^*(b_2)$ with d_{xz}. A qualitative MO diagram for *sym*-$Ni(H_2gma)^-$ showing the orbitals of principal interest is given in Figure 1b.

(48) These are the highest occupied and lowest vacant orbitals in the dinegative ligand. Using the parameters in Table V the next most stable and unstable orbital pairs have energies of 0.5656β and -1.1294β, respectively.

Unlike the case of Ni(gma)$^-$, the differential mixing of $\pi_{\mathrm{L}}{}^*(\mathrm{a}_2)$ and $\pi_{\mathrm{L}}{}^*(\mathrm{b}_2)$ with metal orbitals will depend nearly completely on overlap, rather than on a combination of overlap and relative energy factors. This situation will almost certainly lead to the energy order $\pi^*(\mathrm{a}_2) > \pi^*(\mathrm{b}_2)$ for *sym*-Ni(H$_2$gma)$^-$, compared to $\pi^*(\mathrm{b}_2) > \pi^*(\mathrm{a}_2)$ for Ni(gma)$^-$. Further, the epr results for the former require $\sigma^*(\mathrm{b}_1) > \pi^*(\mathrm{a}_2)$ inasmuch as the observed g tensor does not reveal the near-axial symmetry expected from the $\sigma^{*1}(\mathrm{b}_1)$ configuration. Therefore, the $\ldots\pi^2(\mathrm{b}_2)$, $2\sigma^{*4}(\mathrm{a}_1)$, $\pi^{*2}(\mathrm{b}_2)$, $\pi^{*1}(\mathrm{a}_2)$ ground configuration is assigned to *sym*-Ni(H$_2$gma)$^-$, with the order of orbitals more stable than $\pi^*(\mathrm{a}_2)$ unknown. The proposed appreciable admixture of d_{yz} in this MO results in a situation analogous to the $^2\mathrm{B}_{3g}$ states of [Ni–S$_4$]$^-$ and [Ni–N$_4$]$^-$ and to the $^2\mathrm{B}_g$ state of *trans*-[Ni–S$_2$N$_2$]$^-$, and on this basis could account for the observed g-tensor anisotropy.

Summary

The principal result of this work is the experimental establishment of g-tensor properties for coordinated radical anions. For those complexes assigned the csfr formulation, the measured g tensors suggest the following order of decreasing metal orbital involvement in the odd-electron wave functions: Ni(gma)$^-$ > Ni(dtbh)$^-$ $\sim$ Ni(dbh)$^-$ > Zn(gma)$^-$ $\sim$ Zn(dtbh)$^-$ $\sim$ Cd(gma)$^-$ $\sim$ Cd(dtbh)$^-$. The persisting problem is the establishment of the quantitative degree of metal orbital involvement in these series of complexes which possess, in the phraseology of Schrauzer and Mayweg,[14] "delocalized ground states." In an experimental epr sense, all that can be presently done is to measure the departure of the g tensor from its properties in a cation-stabilized free-radical complex toward those expected for a complex in which the electron is essentially metal-localized. At what point the description is changed from ligand free radical to metal-localized radical is currently a subjective matter.[18] As already emphasized, either description is inadequate and neither supplants a complete molecular orbital treatment including configuration interaction and spin–orbit coupling, which produces a ground state demonstrably reconcilable with experiment.

Acknowledgment. This research was supported by the National Science Foundation under Grants GP-4899 and GP-3398.

Theoretical Aspects of the Linear Enthalpy Wavenumber Shift Relation for Hydrogen-Bonded Phenols[1]

Keith F. Purcell and Russell S. Drago

Contribution from the William Albert Noyes Laboratory, University of Illinois, Urbana, Illinois, and Salem Hall, Wake Forest College, Winston-Salem, North Carolina. Received November 4, 1966

Abstract: The approximation involved in using the observed OH wavenumber shift of phenol upon hydrogen-bond formation as a measure of the magnitude of the interaction has been examined. The equation $-\Delta H = 0.016\Delta\tilde{\nu}_{\mathrm{O-H}} + 0.63$ has been recast in terms of the change in the OH bond energy of phenol on adduct formation, δE_{OH}, and the energy of formation of the new bond between the donor and the hydrogen E_{HB}. The results of molecular orbital calculations (extended Hückel variety) have been analyzed in terms of the bond-energy relationship for the original bond to hydrogen and the hydrogen to base bond. These results provide theoretical justification for the original relationship. Furthermore, this treatment has yielded a parameter which is a quantitative measure of the response of the OH bond of the acid to perturbation by an approaching lone pair of electrons.

In 1962 an enthalpy–OH wavenumber shift ($\Delta\tilde{\nu}_{\mathrm{OH}}$) relationship[2] for phenol adducts was presented which involved a wide range of electron-pair donors. The two experimental quantities were related by the equation

$$-\Delta H\,(\pm 0.5\text{ kcal mole}^{-1}) = 0.016\Delta\tilde{\nu}_{\mathrm{O-H}} + 0.63 \quad (1)$$

The work verified, at least for phenol adducts, the earlier prediction[3] of a linear relationship between the enthalpy of hydrogen-bond formation and OH wavenumber shift. Lippencott and Schroeder[4] several years ago presented a semiempirical model of the hydrogen bond which also predicted a linear relationship between these two quantities over an enthalpy range of -1 to approximately -14 kcal mole^{-1}. A very slight curvature near the origin was predicted which implied a nonzero intercept on the enthalpy axis upon extrapolation of the linear portion of the curve.

More recently, other workers[5,6] have questioned the validity of this linearity. They have studied weak donor systems which apparently do not obey this relationship. In addition it has been stated[5] that there is no theoretical basis for the existence of such a relationship. This uncertainty has stimulated us to examine the theory of frequency shifts from the point of view

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(1) (a) Presented at the 5th National Meeting of the Society for Applied Spectroscopy, Chicago, Ill., 1966; (b) abstracted in part from the doctoral dissertation of K. F. Purcell, University of Illinois, 1965.

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(5) R. West, D. L. Powell, L. S. Whately, M. K. T. Lee, and P. von R. Schleyer, *J. Am. Chem. Soc.*, **84**, 3221 (1962).

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