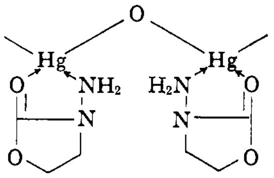
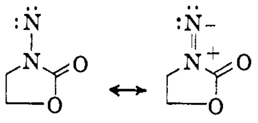
On the basis of the above data, we conclude that compound II is the *trans* isomer and III the *cis* isomer. The mechanism by which III is formed lends support to these assignments, since only with yellow mercuric oxide has it been found possible to isolate the *cis* compound. It is believed that there is a high degree of steric control involved with this unique polymeric[10] oxidant in that it is able to form a highly ordered stereospecific intermediate chelate, of which one possible form is suggested by structure V. Under these conditions, the oxidation and coupling of molecules of I occur while they are held in the *syn* position, resulting in the formation of the *cis* azo structure. With the other oxidants, the uncomplexed aminonitrene (diazene)[11–14] intermediate species VI is probably formed, which due to the lack of any induced stereochemistry collapses by dimerization to the thermodynamically favored *trans* structure.



V



VI

These observations suggest a whole new approach to stereospecific oxidation of 1,1-disubstituted hydrazines. The possibility of designing hydrazines with suitable ligands for complexation and oxidation with yellow mercuric oxide offers the potential of tailor-making a variety of new isomeric azo compounds.

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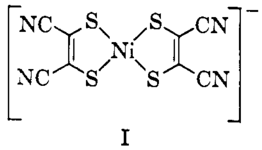
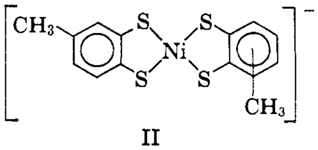
Concerning Cation-Stabilized Anion Free Radicals

Sir:

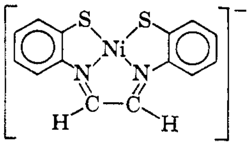
The occurence and the paramagnetic resonance properties of cation-stabilized free radicals are now well documented in the literature.[1–4] In many cases thus far studied the complexed metal ion has a closed-shell configuration, so that extensive mixing of metal and ligand orbitals in the wave function of the unpaired electron is unlikely. It has recently been suggested[5] that several planar anionic complexes, bis(maleonitriledithiolato)nickel ($Ni(mnt)_2^-$, I), bis(toluene-3,4-dithiolato)nickel ($Ni(tdt)_2^-$, II), and glyoxalbis(2-mercaptoanil)nickel ($Ni(gma)^-$, III), are all most appropriately described as containing diamagnetic d^8 Ni(II) with the unpaired electron localized on the ligands. This description was based on the asserted close similarity among the g tensors of these species.[5] Such a suggestion is at variance with the large g-value anisotropy observed for the complexes[6,7] and the demonstration[7] that the Ni(III) d^7 configuration is pragmatically useful in interpreting the oriented single crystal epr properties of $Ni(mnt)_2^-$. The postulated lack of involvement of metal orbitals in the unpaired electron wave functions of these complexes has prompted our extensive paramagnetic resonance investigation of III and related systems. From the point of view of paramagnetic resonance, the ultimate validity of the above postulate hinges upon what is the expected g tensor for a system unambiguously described as a cation-stabilized free radical. Significant deviations of g values from that of a free electron spin ($g = 2.0023$) may be expected from extensive involvement of sulfur orbitals in the wave function.[8]



I



II



III

We have interpreted the g and hyperfine tensor of I in terms of a b_{3g} ground-state wave function, which is roughly 50% delocalized over the π system of the ligands.[7] The spin-orbit coupling was assumed to be entirely caused by the nickel atom, and the contribution of sulfur was not considered. Hückel molecular orbital calculations on I[9] predict considerably less metal

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orbital involvement in the singly occupied orbital. The predicted singly occupied orbital (a_g)[9] cannot be reconciled with the experimental spin Hamiltonian,[7] however.[10,11]

Zn(gma), Cd(gma), and Ni(gma) were prepared by the method of Jadamus, *et al.*[12] In DMF each complex displayed two one-electron reduction waves whose reversibility was established by cyclic voltammetry.[13] The data are given in Table I. (n-Bu_4N)[Ni(gma)] was prepared by reduction of Ni(gma) in THF by sodium amalgam. The complex salt crystallized on addition of n-Bu_4NBr to this solution.[14]

Table I. Peak and Half-Peak Potentials from Cyclic Voltammetry of Glyoxalbis(2-mercaptoanil) Chelates

Chelate[a]	E_p[b]		$E_{p/2}$[b]	
	0 → −1	−1 → −2	0 → −1	−1 → −2
Zn((gma)	−0.92	−1.32	−0.77	. . .
Cd(gma)	−0.91	−1.39	−0.77	−1.28
Ni(gma)	−0.41	−1.21	−0.31	−1.09

[a] Solvent, DMF. [b] Potentials *vs.* aqueous saturated calomel electrode. Peak heights compared with known one-electron reduction, $Ni(mnt)_2^- \rightarrow Ni(mnt)_2^{2-}$.

Paramagnetic resonance measurements were made on electrochemically reduced solutions of the neutral chelates in 50:50 v/v $DMF-CHCl_3$ and $DMSO-CHCl_3$, sodium amalgam reduced solutions in 2-MeTHF, and on solutions of the analyzed salt of III in $DMF-CHCl_3$ and $DMSO-CHCl_3$. These results are shown in Table II.

The anions $Zn(gma)^-$ and $Cd(gma)^-$ can only be formulated reasonably as Zn(II) and Cd(II) with d^{10} closed shell configurations and an anion-radical ligand. The g tensors are isotropic in the glass within our limit of resolution at X-band microwave frequencies and close to that of a free spin. This is the expected result for aromatic free radicals, and is consistent with earlier work on closed-shell cation-stabilized anion-radical ligands.[1,2] Apparently, spin-orbit coupling due to the sulfur atoms does not contribute significantly to the g tensor.

Our results on $Ni(gma)^-$ disagree with those reported by Gray, *et al.*[5] Electroreduction of Ni(gma) in $DMSO-CHCl_3$ and sodium amalgam reduction in 2-MeTHF, as well as *fresh* solutions of the analyzed tetrabutylammonium salt of III in $DMSO-CHCl_3$ *and* $DMF-CHCl_3$, give identical g tensors, which we attribute to authentic $Ni(gma)^-$. Note that this g tensor definitely differs from those of $Zn(gma)^-$ and $Cd(gma)^-$, as do the g tensors of $Ni(mnt)_2^-$ and $Ni(tdt)_2^-$. In addition, we have reproduced the g values reported by Gray, *et al.*,[5] but believe these are due to a decomposition product of III. The radical reported by Gray, *et al.*, can be obtained by (a) electroreduction of Ni(gma) in $DMF-CHCl_3$ and (b) allowing a solution of analyzed (n-Bu_4N)Ni(gma) in $DMF-CHCl_3$ to stand for several days at room temperature. It appears possible that this radical is actually $Ni(o\text{-}C_6H_4S(NH))_2^-$, first reported by us.[15]

Table II. g-values of Glyoxalbis(2-mercaptoanil) and Related Anion Complexes

Complex	Solvent[a]	$\langle g\rangle$[b]	Glass[c]		
			g_1	g_2	g_3
Ni(gma)	$DMSO-CHCl_3$[d]	(2.0030)	1.978	2.005	2.026
Ni(gma)	$DMSO-CHCl_3$[e]	2.0041	1.980	2.004	2.025
Ni(gma)	2-MeTHF[f]	(2.0043)	1.979	2.006	2.028
Ni(gma)	$DMF-CHCl_3$[e]	2.0042	1.975	2.005	2.026
Ni(gma)	$DMF-CHCl_3$[e,g]	2.0560 2.0895 2.106	. . .	. . .	. . .
Ni(gma)	$DMF-CHCl_3$[d]	(2.0527)	2.008	2.022	2.118
$Ni(mnt)_2$	$DMF-CHCl_3$[h]	2.0633	1.996	2.043	2.140
$Ni(tdt)_2$	$DMF-CHCl_3$[i]	2.082	2.016	2.048	2.183
Zn(gma)	$DMF-CHCl_3$[d]	. . .		2.0027[j]	
Zn(gma)	2-MeTHF[f]	. . .		2.0033[j]	
Cd(gma)	2-MeTHF[f]	. . .		2.0024[j]	

[a] Mixed solvents are 50:50 v/v. [b] Solution (isotropic) g value. Parentheses indicate value calculated from glass data. [c] Glasses run at ~85°K. [d] Anion generated by controlled potential electrolysis. [e] Solution made from analyzed sample of (n-Bu_4N)Ni(gma). [f] Anion prepared by sodium amalgam reduction. [g] Measured after solution stood 5 days at room temperature. Signals from three distinct radicals are identified. [h] From ref 6. [i] From ref 5. [j] g values isotropic in glass. Spectra also show additional lines and a half-field resonance compatible with a triplet species; see text.

Further evidence that $Ni(gma)^-$ is electronically dissimilar to $Cd(gma)^-$ and $Zn(gma)^-$ is afforded by the reversible reduction potentials assembled in Table I. The difference of *fully 0.5 v* in the first reduction potential of Ni(gma) and that of the Zn and Cd chelates is evidence that the same anion-radical description is not common to all three.[16]

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(9) S. I. Shupack, E. Billig, R. J. H. Clark, R. Williams, and H. B. Gray, *J. Am. Chem. Soc.*, **86**, 4594 (1964).

(10) It should be noted that the x and y axes of the complex are interchanged in ref 7 and ref 9. Thus the b_{3g} representation in ref 7 becomes the b_{2g} representation of ref 9.

(11) G. N. Schrauzer and V. P. Mayweg, *J. Am. Chem. Soc.*, **87**, 3585 (1965), using a molecular orbital theory similar to ref 9, but with a different set of initial assumptions, found that the highest occupied molecular orbital of $NiS_4C_4H_4^{=}$ has b_{3g} symmetry in agreement with the conclusion from the paramagnetic resonance of oriented samples of I. The b_{3g} orbital was found by Schrauzer and Mayweg to have approximately 18% metal character which, although small, is consistent with the reduced magnitudes of the spin Hamiltonian parameters of I.[7]

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(13) We are grateful to K. Darlington for the cyclic voltammetry measurements.

(14) *Anal.* Calcd for $NiC_{30}H_{46}N_3S_2$: 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.

(15) A. L. Balch, F. Röhrscheid, and R. H. Holm, *J. Am. Chem. Soc.*, **87**, 2301 (1965); note the considerable similarity between the g tensors for this complex and the alleged $Ni(gma)^-$ in ref 5.

(16) If it is claimed that $Ni(gma)^-$ is properly described as Ni(II)–radical–ligand, and that $Zn(gma)^{-1}$ and $Cd(gma)^-$ are similarly Zn(II)–radical–ligand and Cd(II)–radical–ligand, then electroreduction of all three neutral chelates involves the single occupancy of the lowest lying empty ligand orbital. We assume throughout that this ligand orbital does not mix significantly with metal orbitals. The half-wave potential for the reduction varies with the one-electron energy of the molecular orbital in question, and in this model this varies only by the difference in the interaction energy of the electron and the metal atom. This interaction energy should be closely the same, using this model of a "closed-shell" dipositive central ion in each case. Thus, the 0.5-v difference in the reduction potential between Ni(gma) *vs.* Zn(gma) and Cd(gma) is difficult to justify on the basis of the description of all three anions being M(II)–radical–ligand. Since it is more reasonable that this is a proper description for Zn and Cd (noting the close agreement of the reduction potentials), we conclude that $Ni(gma)^-$ should not be described this way, and that the orbital filled by electroreduction is most probably a mixture of ligand and metal character. In an earlier communication[3] we obtained evidence from paramagnetic resonance measurements that in the electrooxidation ($n = -2 \rightarrow n =$

We have been able to prepare Zn(gma) as blue and red forms. The blue form is soluble in DMF but a red form soon precipitates and is probably polymeric, or at least dimeric material. The single isotropic resonance in glasses of reduced blue material (which we attribute to the monomer) invariably is accompanied by satellites attributable to zero-field splitting in a molecular triplet state. A half-field $\Delta M_S = 2$ transition is also observed. These observations are consistent with our suggestion of polymerization in these systems.

We have shown that in the complex Ni(gma)$^-$, the deviation of the principal g values from that of a free spin is a result of the participation of metal orbitals in the molecular orbital of the odd spin. The isotropic g values of Zn(gma)$^-$ and Cd(gma)$^-$, which are both properly described as containing radical ligands, are almost identical with that of a free electron. This result demonstrates that spin–orbit coupling due to ligand atoms does not lead to large g shifts in these complexes. The larger g shifts for Ni(mnt)$_2^-$ and Ni(tdt)$_2^-$ suggest that the metal orbital participation in the half-filled molecular orbital is larger than in Ni(gma)$^-$. Therefore, the description[5] of all three anions as Ni(II)–radical–ligand complexes is oversimplified, and the basis on which it was proposed (*i.e.*, the supposed similarity of the g tensors of the three Ni anions) is vitiated by the present investigation. We suggest that g tensors which are isotropic and close to that of a free electron are diagnostic evidence for cation-stabilized radicals in these and similar thio ligand systems. It is clear that what is needed is a theory which will allow the quantitative interpretation of spin-Hamiltonian parameters for systems where there is extensive delocalization of the unpaired electrons over the ligands. This is a formidable theoretical problem, but its solution would help to cast further light on the electronic structures of many interesting paramagnetic chelates.

Acknowledgment. This work was supported by the National Science Foundation.

−1) of the diamagnetic six-coordinate complexes MoS$_6$C$_6$(CF$_3$)$_6^n$ and WS$_6$C$_6$(CF$_3$)$_6^n$, the electron is removed from a ligand-localized orbital. We found that the oxidation half-wave potentials were +0.36 to +0.32 v, respectively, further supporting our argument that the particular metal atom has little effect (except by its charge) on the oxidation–reduction potential when a ligand electron is involved.

[17] National Institutes of Health Predoctoral Fellow.

[18] (a) Alfred P. Sloan Foundation Fellow; (b) NSF Predoctoral Fellow, 1963–1966.

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Received December 9, 1965

Structural Characterization of a New Niobium Subhalide, Nb$_6$I$_{11}$, Containing the First Known [M$_6$X$_8$]^n Group with Nonintegral Metal Oxidation State

Sir:

Considerable experimental and theoretical work[1–17] recently has been directed toward the characterization of niobium and tantalum subhalides, in which for several phases the structures have a common hexanuclear metal building block of stoichiometry [M$_6$X$_{12}$]^n (with $n = +2$, $+3$, and $+5$(?) reported in the solid state and $n = +2$ and $+4$ in solution). These hexameric ions of niobium and tantalum, containing an octahedral metal framework with halogen atoms bridging the edges, exhibit unusually rich electronic spectra characteristic of polynuclear metal complexes with strong metal–metal interactions.

We wish to report the structural determination of a new polynuclear niobium metal cluster Nb$_6$I$_{11}$, which as the lowest found niobium subhalide contains the first [M$_6$X$_8$]^n species observed for the group V transition elements. The identity of Nb$_6$I$_{11}$ was established by an X-ray investigation of a single crystal from a sample of Nb$_3$I$_8$,[1] generously furnished to us by Professor J. D. Corbett and Dr. M. A. Kust of Iowa State University (Ames), which had been partially disproportionated during a transpiration study of vaporization. The phase NbI$_{1.83}$ (or Nb$_6$I$_{11}$) first was isolated by Schäfer and Simon[7,14] who proposed as most probable the correct structural formula [Nb$_6$I$_8$]$^{3+}$(I$^-$)$_3$.

The compound crystallizes in an orthorhombic unit cell with symmetry Pccn ($D_{2h}{}^{10}$) and lattice parameters $a = 15.31 \pm 0.03$, $b = 11.34 \pm 0.03$, and $c = 13.58 \pm 0.03$ A. Considerable difficulty was encountered in obtaining a suitable single crystal for X-ray measurements owing to moisture sensitivity and crystal twinning problems. The subsequent structural determination revealed four formula species of Nb$_6$I$_{11}$ per unit cell with $\rho_{\text{calcd}} = 5.21$ g cm^{-3}. After unsuccessful attempts to interpret Patterson and superposition maps for the presumed Nb$_3$I$_8$, both the configuration and correct composition were elucidated by the application of a symbolic addition method of phase determination.[18] The present anisotropic least-squares refinement gives $R_1 = 9.8\%$ and $R_2 = 10.2\%$ for the 1087 observed, independent reflections collected photographically with Mo Kα radiation.

The structure consists of [Nb$_6$I$_8$]$^{3+}$ groups with a configuration (Figure 1) in which the six niobium atoms are arranged octahedrally about a crystallographic center of symmetry with the eight iodine atoms symmetrically located above the triangular faces.

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