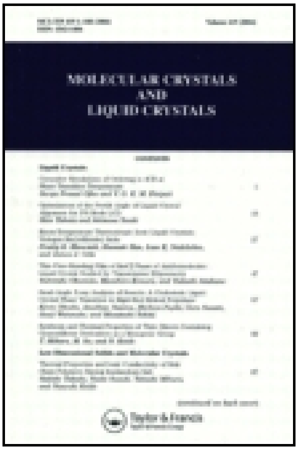

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ESR and Theoretical Studies of Bis-Benzene-1, 2-Diselenolate Nickel and Related Complexes

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ESR AND THEORETICAL STUDIES OF BIS-BENZENE-1,2-DISELENOLATE NICKEL AND RELATED COMPLEXES

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Abstract ESR and theoretical studies of the transition metal complexes of [Co and Ni(Se$_2$C$_6$H$_4$)$_2$]$^-$(n-C$_4$H$_9$)$_4$N$^+$ are reported and compared with closely related systems. Room temperature single crystal X-ray studies reveal the Nickel complex is orthorhombic. ESR studies of the polycrystalline powders of the Ni complex as a function of temperature from 108 K to room temperature show a series of spectral envelopes which can arise only from a paramagnetic site which possesses axial symmetry. At *ca* 160 K, there is an abrupt change in the value of the principal components of the anisotropic g-tensor of the Ni complex which is discussed. Low temperature ESR studies of polycrystalline samples of the ground state triplet Cobalt complex which is isomorphous with the Nickel complex reveal an orthorhombic g-tensor. From the field position of the half-field resonance, it is possible to calculate a mean separation, of the two electrons which make up the triplet state, of 4.3(±0.5) A.

INTRODUCTION

We have previously reported details of the synthesis[1] and of physical studies[2] of bis-benzene 1,2-diselenolate(bds) transition metal(Co, Ni and Cu) complex monoanions which have been isolated and studied as the tetra-n-butyl-ammonium salt. We now report additional physical studies and the results of extended Huckel molecular orbital calculations on the Co and Ni complexes and related sulfur containing analogs.

EXPERIMENTAL RESULTS

$\mathrm{Cobalt(bds)_2^-}$

Static magnetic susceptibility measurements which we previously reported[2] have established that the electronic ground state of the cobalt complex is a triplet. However, we had been unable to observe its electron spin resonance(ESR) spectrum. Recent low temperature(10 K) ESR experiments have allowed us to observe the polycrystalline ESR spectral envelope of $\mathrm{Co(bds)_2^-}$.

Our ESR results, which are summmarized in Table 1, show that the electronic ground state does not arise from an orbitally degenerate state(i.e., from a state possessing E type symmetry) because the g-tensor is orthorhombic. Note, this is in contradiction to an earlier interpretation of the observation that the cobalt salt possesses a triplet ground state[2]. We have observed, also, the half-field resonance($\Delta m = 2$) at $g = 2.157$. While the triplet nature of the ground state of this complex has already been established by static magnetic susceptibility measurements, this observation is pleasing, independent, confirmation of our earlier work.

If one uses the analysis of de Groot and van der Waals[3], it is possible, from the knowledge of the value of the magnetic field at which the half-field resonance occurs, to estimate the value of D, the spin-spin dipolar coupling parameter, and hence the mean separation of the two electrons which form the triplet state[4]. Our analysis

TABLE 1 Principal components of the g-tensor at 10 K for $Co(bds)_2^-$ compared to those at room temperature for $Ni(bds)_2^-$.

g	$Co(bds)_2^-$	$Ni(bds)_2^-$
g_1	2.249(±1)	2.1723(±1)
g_2	2.096(±1)	2.1723(±1)
g_3	2.045(±1)	2.0765(±1)
<g>	2.130(±1)*	2.1404(±1)

*The $\Delta m = 2$ transition occurs at g = 2.157(+14) where ν = 9.298 GHz

yields a value for D of 0.0335 cm^{-1}(357 G) and hence a mean separation of 4.3(±0.5) A. We shall discuss these data in more detail following a presentation of the results of the Extended Huckel molecular orbital calculations.

Nickel$(bds)_2^-$

Both ESR and static magnetic susceptibility measurements have established that the electronic ground state of this complex is a doublet[2]. Moreover, based on anisotropic g-tensor measurements as a function of temperature this ground state is found to possess axial symmetry. However, as shown in Figures 1 and 2 of ref. 2, there is a rather abrupt change in the values of the perpendicular components of the g-tensor at ca 160 K. This change is not accompanied by a corresponding abrupt change in the magnetic susceptibility. However, differential scanning calorimetry measurements confirm a transition at this temperature with a heat of transition of 1.09 KJ/mole. We have concluded on the basis of these results that the tetra-n-butylammonium nickel bis-1,2-diselenolate complex undergoes a phase transition at this temperature. Low temperature X-ray studies are planned to study this point.

EXTENDED HUCKEL MOLECULAR ORBITAL CALCULATIONS

Extended Huckel molecular orbital calculations[5] have been utilized to determine the order of the electronic energy levels, composition of the molecular orbitals, the total charge density distribution(i.e., Mulliken population analysis) as well as the charge density distribution within the orbitals which contain the unpaired electrons of the Co and Ni(bds) and bis-1,2-dithiolato(bdt) complexes.

The extended Huckel calculation is based on the Wolfsberg-Helmholz expression for the resonance integral, H_{uv}, in which the basis set of

$$H_{uv} = kS_{uv}(H_{uu} + H_{vv})/2$$

orbitals is comprised of all valence shell orbitals regardless of occupation[6]. Contracted d orbitals were used for the transition metal atoms.

The input required to evaluate the resonance integral includes atomic coordinates, appropriate values for the coulomb or valence orbital ionization energy(VOIE), H_{xx}, and the appropriate selection of the value for k. The atomic positions were obtained from the crystallographic data for Ni(bds)$_2$. The Co and Ni complexes, which are isomorphous, were assumed to have identical atomic coordinate positions as were their respective bdt complexes. K was chosen to be 1.75. The VOIES were obtained to, a large extent, from the program documentation. The values of VOIES used for selenium were 20.8, 10.8 and 7.8 ev for the s, p and d valence orbitals, respectively, and are consistent with those reported for sulfur.

Since the VOIES have a significant charge dependence, iterative methods which provide for first order correction of the VOIE due to the molecular charge have been used. This charge iteration is based on a linear dependence of the VOIE on the molecular charge.

$$H_{ii} = H_{ii}^{o} + (\text{sense}) * \text{charge}$$

In this expression, H_{ii}^{o} is the VOIE for the neutral atom, the charge is the molecular charge, and the sense is the slope.

The electron density distribution(which to first approximation is proportional to the unpaired spin density distribution) for Co and Ni(bds)$_2^-$ and for Co and Ni(bdt)$_2^-$ obtained from the Extended Huckel molecular orbital calculations are given in Tables 2 and 3, respectively, for the orbital(s) which contain the unpaired electron(s). The corresponding total electron density distributions are given in Tables 4 and 5.

TABLE 2 Extended Huckel Electron Density Distribution in the Orbitals which contain the Unpaired Electrons for M(bds)$_2^-$ (See Figure 1 for numbering of atomic positions).

	Co(bds)$_2^-$		Ni(bds)$_2^-$
Atom	Orbital 1*	Orbital 2*	HOMO
M(Co/Ni)	0.879	0.221	0.178
Se	0.030	0.149	0.148
C(1)	0.000	0.001	0.002
C(2)	0.000	0.032	0.038
C(3)	0.000	0.013	0.017

*As Co(bds)$_2^-$ has a triplet ground state, the two electrons must reside in two different orbitals. Orbital 1 has the lower energy of the two.

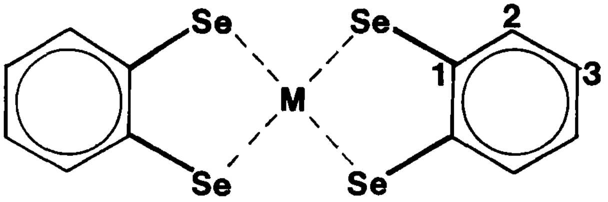

Figure 1 Position Numbering for M(bds)$_2^-$

TABLE 3 Extended Huckel Electron Density Distribution in the Orbitals which contain the Unpaired Electrons for $M(bdt)_2^-$ (See Figure 1 for numbering of atomic positions).

	$Co(bdt)_2^-$		$Ni(bdt)_2^-$
Atom	Orbital 1*	Orbital 2*	HOMO
M(Co/Ni)	0.786	0.152	0.111
S	0.053	0.174	0.178
C(1)	0.000	0.000	0.000
C(2)	0.000	0.026	0.031
C(3)	0.000	0.010	0.013

*As $Co(bdt)_2^-$ has a triplet ground state, the two electrons must reside in two different orbitals. Orbital 1 has the lower energy of the two.

DISCUSSION AND CONCLUSIONS

$Co(bds)_2^-$ and $Co(bdt)_2^-$

As noted above, an analysis of the position of the half field resonance line for the $Co(bds)_2^-$ complex leads to the result that the two electrons of the triplet ground state have a mean separation of ca 4.3 A and the conclusion that both of the orbitals which these two electrons occupy can not be centered predominately on the transition metal, otherwise, the observed mean separation of the two electrons would be smaller. The calculated electron distributions shown in Tables 2 and 3 are quite consistent with our experimental results(i.e., the electron density of the lowest energy orbital of the two is centered predominately upon the transition metal whereas that of the higher energy orbital is centered mostly upon the selenium atoms of the ligand).

TABLE 4 Extended Huckel Total Charge Density Distribution in $M(bds)_2^-$ where M = Co and Ni(See Figure 1 for Position Numbering)(See Figure 1 for numbering of atomic positions).

Atom	Complex	
	$Co(bds)_2^-$*	$Ni(bds)_2^-$
M(Co/Ni)	+2.042	+2.460
Se	-0.401	-0.481
C(1)	-0.263	-0.227
C(2)	-0.024	-0.079
C(3)	-0.119	-0.126
H(2)	+0.020	+0.020
H(3)	+0.027	+0.027

*The total charge distribution in $Co(bds)_2^-$ is calculated by taking into account that the two highest occupied orbitals contain one electron each.

We are struck by the similarity of the molecular orbitals which contain the unpaired electrons in these two cobalt complexes as well as by the similarity of their calculated total charge distribution. It is also noteworthy that the electron distribution in the higher energy molecular orbital of each the cobalt complexes is very similar to that calculated for the corresponding monoanion nickel complexes. This has caused us to initiate additional experimental work involving the bdt complexes as well as the dianion of the cobalt complexes since, on the basis of the molecular orbital calculations, we expect the cobalt dianion and nickel monoanion bds and bdt pairs to exhibit similar ESR behavior. The results of these studies will be reported upon in the future.

TABLE 5 Extended Huckel Total Charge Density Distribution in $M(bdt)_2^-$ (See Figure 1 for numbering of atomic positions).

Atom	Complex	
	$Co(bdt)_2^-$*	$Ni(bdt)_2^-$
M(Co/Ni)	+1.570	+2.028
S	-0.238	-0.315
C(1)	-0.306	-0.284
C(2)	-0.061	-0.080
C(3)	-0.146	-0.157
H(2)	+0.023	+0.023
H(3)	+0.056	+0.056

*The total charge distribution in $Co(bdt)_2^-$ is calculated by taking into account that the two highest occupied orbitals contain one electron each.

$Ni(bds)_2^-$ and $Ni(bdt)_2^-$

Two features of the $Ni(bds)_2^-$ ESR study stand out. One is the phase transition at ca 160 K which is still being studied. The second is the observation that the g-tensor is axial even though the molecule possesses only two fold rotational symmetry. The calculated electron density distribution in the highest occupied orbital for $Ni(bds)_2^-$ leads us to an explanation of this observation(See Table 4). Most of the unpaired electron(hence the spin) density is symmetrically distributed over the nickel and the four selenium atoms. Thus, to first order, the unpaired electron distribution about the nickel is square planar(i.e., axial). As noted earlier, based on our molecular orbital calculations we expect similar behavior for $Ni(bdt)_2^-$ and the dianions of the two cobalt complexes.

XPS experiments on the bds and bdt complexes are underway at the University of Missouri-St. Louis to better understand the oxidation state of the metal ions in these complexes and their electronic structure and spectra.

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