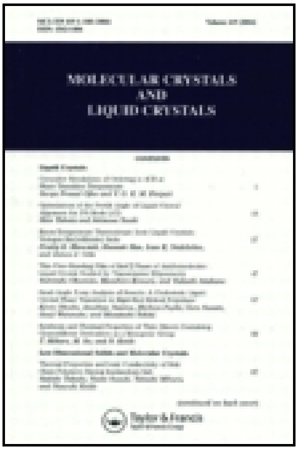

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Magnetic Studies of New Linear Chain Transition Metal Diselenolenes

D. J. Sandman [a], J. C. Stark [a], G. Allen [a], L. A. Acampora [a], M. T. Jones [b], S. Jansen [b] & G. J. Ashwell [c]

[a] GTE Laboratories Incorporated, 40 Sylvan Road, Waltham, MA, 02254, U.S.A.

[b] Department of Chemistry, University of Missouri-St. Louis, St. Louis, Missouri, 63121, U.S.A.

[c] Department of Chemistry, Sheffield City Polytechnic, Sheffield, SI 1WB, England

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MAGNETIC STUDIES OF NEW LINEAR CHAIN TRANSITION METAL DISELENOLENES

D. J. SANDMAN, J. C. STARK, G. ALLEN, L. A. ACAMPORA
GTE Laboratories Incorporated, 40 Sylvan Road, Waltham, MA 02254, U.S.A.
M. T. JONES, S. JANSEN
Department of Chemistry , University of Missouri-St. Louis, St. Louis, Missouri 63121, U.S.A.
G. J. ASHWELL
Department of Chemistry, Sheffield City Polytechnic, Sheffield S1 1WB, England

Abstract The o-benzenediselenolate dianion(bds) reacts with transition metal dichlorides(Co, Ni, Cu) to give new transition metal diselenolenes isolated as tetra-n-butylammonium salts. These materials have been characterized by elemental analysis, cyclic voltammetry, electronic spectroscopy, x-ray diffraction, ESR and static magnetic susceptibility. The crystal structure of $(n\text{-}C_4H_9)_4N^+Ni(bds)_2^-$ reveals a mixed chain structure. This report primarily presents the results of studies of the magnetic properties of Co, Ni and Cu diselenolenes as revealed by ESR and static magnetic susceptibility techniques.

INTRODUCTION

Transition metal dithiolenes are multistage redox systems that have received considerable attention over the last twenty years for aspects of their unusual chemical bonding as well as their structural, electrical and magnetic properties[1]. While the number of square planar dithiolenes which have been prepared is very large, the analogous selenium substances, the diselenolenes, are comparatively rare. We report the results of physical studies, particularly, magnetic studies, of a series of transition metal diselenolenes where the metals are Co, Ni and Cu.

SYNTHESIS

The metal bis-diselenolenes are prepared from poly-o-phenylenediselenide and converted to the tetra-n-butyl salt of the appropriate transition metal o-benzenediselenoate(bds). The metals studied to date include cobalt, nickel and copper. The synthesis route is summarized in Reference 2.

ESR AND MAGNETIC SUSCEPTIBILITY STUDIES

$Nickel(bds)_2^-$

Studies of the ESR spectral envelope of polycrystalline samples of the nickel salt demonstrate that the paramagnetic site possesses axial symmetry over the entire temperature range of the study(i.e., 108 to 298 K). The values of the principal components of the g-tensor were obtained by the method described by Kneubuhl[3] and are shown in Figure 1. At a few repre-

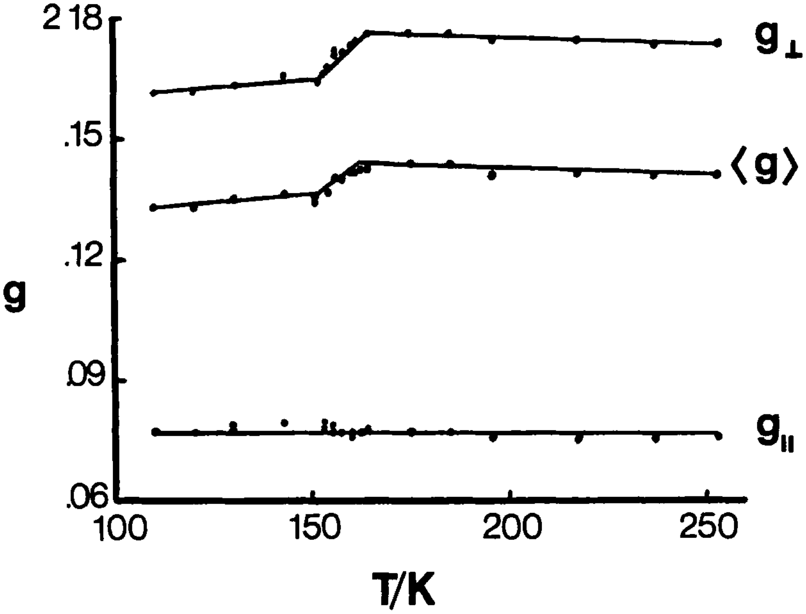

FIGURE 1 g-Tensor components for $(n\text{-}C_4H_9)_4N^+Ni(bds)_2^-$ as a function of temperature.

sentative temperatures, the values of the principal components of the g-tensor were used to simulate the expected spectral envelope using a program developed in our laboratory[4]. The simulation confirms the accuracy of the g-tensor components reported here. At approximately 160 K, there is an abrupt change in the perpendicular component of the g-tensor as shown in Figure 1. Although, relative ESR signal intensity measurements suggested that there might be a change in the magnetic susceptibility at this temperature, static susceptibility measurements show conclusively that the nickel salt follows Curie law from 20 to 300 K and possesses only one unpaired electron per anion with a magnetic moment of 1.94 Bohr magnetons. Other physical studies of this transition are in progress and will be reported when completed. In Figure 2, the ESR spectral envelopes of tetra-n-butyl ammonium nickel(bds)$_2$ at temperatures above and below the transition temperature are shown.

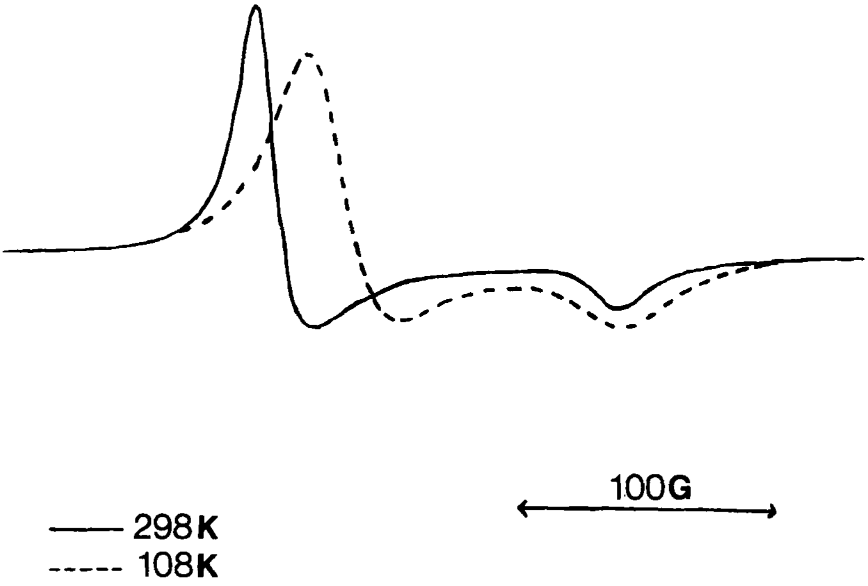

FIGURE 2 ESR envelope of Ni(bds)$_2^-$ above and below the transition temperature.

Cobalt$(bds)_2$ and Copper$(bds)_2$

ESR spectra could be not observed for the cobalt and copper analogs of $(C_4H_9)_4N^+Ni(bds)_2^-$ in the temperature range, 108 to 298 K. Static magnetic susceptibility measurements from 20 to 300 K confirm that the copper salt is diamagnetic and that the cobalt compound possesses two unpaired electrons per anion with a magnetic moment of 3.43 Bohr magnetons. The cobalt salt follows Curie law from 4.2 to 300 K. Our inability to observe the ESR spectrum of the cobalt salt is consistent with previously reported studies of cobalt complexes and is attributed to their extremely short spin lattice relaxation times. ESR studies on the cobalt salt at liquid helium temperatures are planned.

SUMMARY OF MAGNETIC DATA

g-Tensor

Table 1 compares the principal components of the g-tensor of $Ni(bds)_2^-$ with those of two related compounds(i.e., the sulfur analog, labeled bdt, and a mixed sulfur-selenium ligand).

TABLE 1 Principal components of the g-tensors at T=300 K for $Ni(bds)_2^-$ and related compounds.

	Ligands		
g	bdt[5]	Mixed S/Se[6]	bds
g_1	-	2.228	2.1723
g_2	-	2.086	2.1723
g_3	-	2.034	2.0765
$\langle g \rangle$	2.0779	2.116	2.1404

Magnetic Moments

Table 2 lists the moments observed for the sulfur and selenium analogs of the Co and Ni salts.

TABLE 2 Summary of magnetic moments in Bohr magnetons.

Ligand	Metal	
	Cobalt	Nickel
bdt[8]	3.27	1.83
bds	3.43	1.94

X-RAY STRUCTURE[2]

Crystals of $(C_4H_9)_4N^+Ni(bds)_2^-$ are orthorhombic, space group $Pbc2_1$, Z=4, with a = 9.904(3), b = 16.954(5), and c = 19.106(6)A. Full matrix least squares refinement of positional and thermal parameters for all non-hydrogen atoms, using 1029 data for which F is greater than 3.92 (F), led to R = 0.065, Rw = 0.068. The $NiSe_4$ unit is square planar within experimental error, with an average Ni-Se distance of 2.259A. The packing of the molecular anions and cations is shown in Reference 2. The anions are well separated; there are no short Ni---Se contacts. Further, there are no Se---Se contacts at distances less than 5.0A. The cobalt salt is isomorphous with the nickel salt. Polycrystalline samples of the copper salt are a mixture of at least two phases one of which is isomorphous with the nickel and cobalt salts[7].

ELECTRONIC SPECTRAL DATA

Table 3 compares and summarizes the major electronic spectral bands for the bds and bdt salts.

DISCUSSION

Figure 3 shows the isotropic g-tensor for the homologous series of the nickel complexes described in Table 1 plotted against the mean spin-orbit interaction parameter of the respective chalcogen atom. An analysis of this data can be made using equation (1).

$$g = g_o + b \cdot S_o \qquad (1)$$

TABLE 3 Major, intense spectral bands for the cobalt, nickel, and copper bdt[8] and bds complexes in cm^{-1}.
(Molar extinction coefficients are in parenthesis)

$Co(bdt)_2^-$	$Ni(bdt)_2^-$	$Cu(bdt)_2^-$
15,200(12,100)	11,350(13,200)	25,400(30,000)

$Co(bds)_2^-$	$Ni(bds)_2^-$	$Cu(bds)_2^-$
12,510(1100)	10,360(3200)	24,528(19,000)
13,804(2000)	11,800(4300)	31,670(4600)
14,717(1600)		
17,681(1600)		
25,316(7000)		
29,434(8200)		

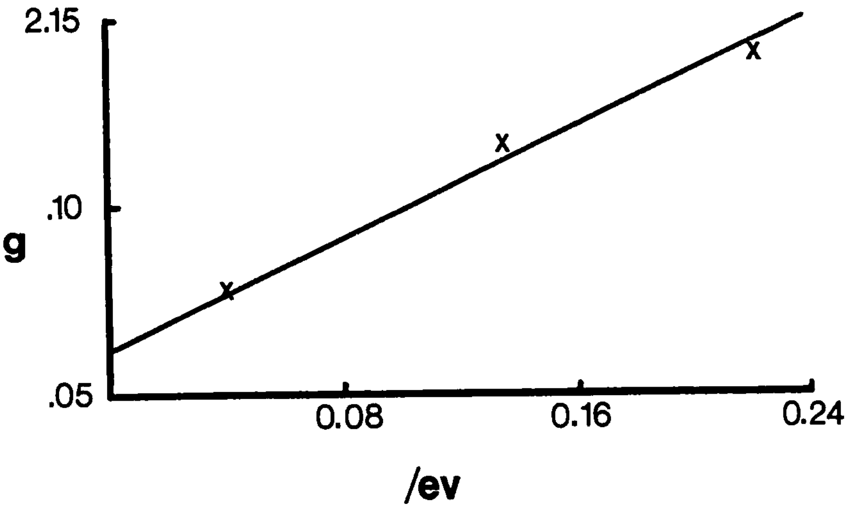

FIGURE 3 Isotropic g-values plotted against spin orbit interaction energies of the chalcogen atoms.

In this equation, g_o is the isotropic g-tensor for the homolog for which the chalcogen atoms have no spin-orbit interaction energies, b is the slope and S_o is the mean spin-orbit interaction energy of the chalcogen atoms of the appropriate salt. A least squares fit of the data used in Figure 3 yields:

$$g_o = 2.0618$$

$$b = 0.3677$$

S_o=0.050 and 0.22 ev. for the sulfur and selenium, respectively.

This analysis also allows one to estimate the contribution to the isotropic g-tensor from the spin-orbit interaction energy due to the presence of the Nickel ion in the salt which is approximately the difference between g_o and the free electron g. This analysis yields a value of $\Delta g = 0.0595$.

The magnetic moment varies as the square of the isotropic g-value. Thus, it is of interest to compare the ratio of the magnetic moments of $Ni(bds)_2^-$ and $Ni(bdt)_2^-$(1.06) shown in Table 2 with the ratio of the square of their respective isotropic g-values(1.06) taken from Table 1.

The static magnetic susceptibility data on $Co(bds)_2^-$ and $Ni(bds)_2^-$ clearly indicate there is no cooperative magnetic interaction between paramagnetic spin sites in either complex(i.e., each spin acts independently of all of its neighbors). This is consistent with the observed crystal structure of these complexes in which each magnetic entity is physically rather far from its nearest neighbor. Moreover, since the electron spin quantum number(S) is equal to 1 for $Co(bds)_2^-$ and the the magnetic susceptibility obeys Curie law from 20 to 300 K, the electronic ground state must be absolutely orbitally degenerate in this temperature range. There is absolutely <u>no</u> indication of thermal averaging over two near orbitally degenerate states in this temperature range for $Co(bds)_2^-$.

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

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