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Single-Crystal and Powder EPR Study on Tetra-*n*-butylammonium Bis(2-thioxo-1,3-dithiole-4,5-diselenolato)cuprate(II), $(n\text{-Bu}_4\text{N})_2[^{63}\text{Cu(dsit)}_2]$, Doped into $(n\text{-Bu}_4\text{N})_2[\text{Ni(dsit)}_2]$

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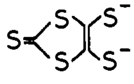
A single-crystal and powder EPR study of tetra-*n*-butylammonium bis(2-thioxo-1,3-dithiole-4,5-diselenolato)cuprate(II), $(n\text{-Bu}_4\text{N})_2[\text{Cu(dsit)}_2]$, incorporated in the corresponding Ni(II) complex is reported. The directions of the principal axes of the ^{63}Cu and ^{77}Se hyperfine splitting tensors and the magnitudes of their components agree with what is expected for a planar complex of approximately D_{2h} symmetry with one unpaired electron in an antibonding σ-type molecular orbital. Two principal axes of the g tensor do not coincide with the corresponding Cu hfs tensor axes. The hfs data were used to estimate the delocalization of the unpaired electron.

Introduction

During the last few years, metal bis complexes of the ligand 2-thioxo-1,3-dithiole-4,5-dithiolate (dmit, **1**; from the notation dimercaptoisotrithione used primarily) attracted a growing interest because of the electronic and magnetic properties.[1-5] Furthermore, some interesting electric properties have also been observed: $\text{TTF[Ni(dmit)}_2]$ (TTF = tetrathiafulvalene) is a superconductor characterized by 10^5 S cm^{-1} at $T = 4$ K.[6]

Single-crystal EPR studies on $(n\text{-Bu}_4\text{N})_2[\text{Cu(dmit)}_2]$ showed highly covalent Cu–S bonds.[4] The spin density distribution was estimated by using ^{33}S ligand hfs data (hfs = hyperfine structure). The accuracy, however, is limited because of (a) the low natural abundance of the isotope ^{33}S (only 0.74%) and (b) the smallness of the couplings usually observed.

Extending our investigations on chalcogeno-rich metal complexes, we recently prepared a series of metal complexes of the analogous new selenium ligands 2-selenoxo-1,3-diselenole-4,5-diselenolate[7] (dsis, **2**) and 2-thioxo-1,3-dithiole-4,5-diselenolate[8,9] (dsit, **3**). Copper(II) complexes of these ligands will be more favored for EPR studies because the natural abundance of the selenium isotope ^{77}Se ($I = {}^1/_2$) is, at 7.5%, a factor 10 larger than that of ^{33}S. Furthermore, the ^{77}Se hfs couplings are expected to be considerably larger than the corresponding ^{33}S ones.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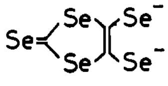
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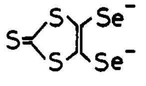
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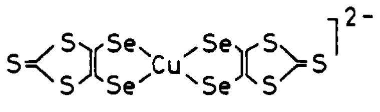
In this paper, we report the first single-crystal EPR study as well as the powder EPR spectrum on a diselenolene complex: tetra-*n*-butylammonium bis(2-thioxo-1,3-dithiole-4,5-diselenolato)cuprate(II), $(n\text{-Bu}_4\text{N})_2[\text{Cu(dsit)}_2]$ (**4**), diamagnetically diluted by the corresponding Ni(II) chelate. Up to now for copper(II) diselenole complexes only the liquid-solution EPR spectrum of bis(1,2-trifluoromethylethylene-1,2-diselenato)cuprate(II)[10] has been reported. To simplify the spectra, isotopically enriched Cu is used.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The EPR parameters obtained are used to get a detailed picture of the spin-density distribution in the molecular orbital (MO) of the unpaired electron and to obtain information about the molecular structure. Furthermore, the EPR parameters will be compared with those of $[\text{Cu(dmit)}_2]^{2-}$ and those of the bis(dialkyldiselenocarbamato)copper(II) complexes,[11-13] which also contain a CuSe_4 coordination sphere.

Experimental Section

$(n\text{-Bu}_4\text{N})_2[^{63}\text{Cu(dsit)}_2]$ and $(n\text{-Bu}_4\text{N})_2[\text{Ni(dsit)}_2]$ were prepared according to the method described by Olk et al.[9] For the preparation of the Cu complex, ^{63}Cu-enriched $\text{CuCl}_2\cdot 2\text{H}_2\text{O}$ was used (enrichment: 97.8% ^{63}Cu).

Suitable single crystals and powders of $(n\text{-Bu}_4\text{N})_2[^{63}\text{Cu/Ni(dsit)}_2]$ containing about 0.5 mol % of the Cu guest complex were grown at room temperature by slow solvent evaporation from acetone/pyridine solutions under argon atmosphere.

The EPR spectra were recorded on a Varian E-112 spectrometer in the X-band at room temperature. Three perpendicular planes were measured; spectra were taken every 5°. The spin-Hamiltonian parameters were determined by using the universal program MAGRES.[14] The deviations between the experimental and simulated line positions after the fitting procedure were smaller than 0.2 mT. The simulation of the powder spectrum was done with MAGRES also.

Results and Discussion

The structure of $(n\text{-Bu}_4\text{N})_2[\text{Ni(dsit)}_2]$ is known.[15] $(n\text{-Bu}_4\text{N})_2[\text{Ni(dsit)}_2]$ was found to be isomorphic with the corresponding "all-sulfur" complex $(n\text{-Bu}_4\text{N})_2[\text{Ni(dmit)}_2]$[16] and crystallizes in the monoclinic space group $P2_1/c$, with two molecules per unit cell. The complex anion is nearly planar; Ni occupies an inversion center.

The general features of the angular dependence of the single-crystal EPR spectra of $(n\text{-Bu}_4\text{N})_2[^{63}\text{Cu/Ni(dsit)}_2]$ are similar to those earlier observed for the $(n\text{-Bu}_4\text{N})_2[\text{Cu/Ni(dmit)}_2]$ system[4] and confirm the isomorphy between the Ni complexes. As expected, the EPR spectra show the absorption peaks of two mag-

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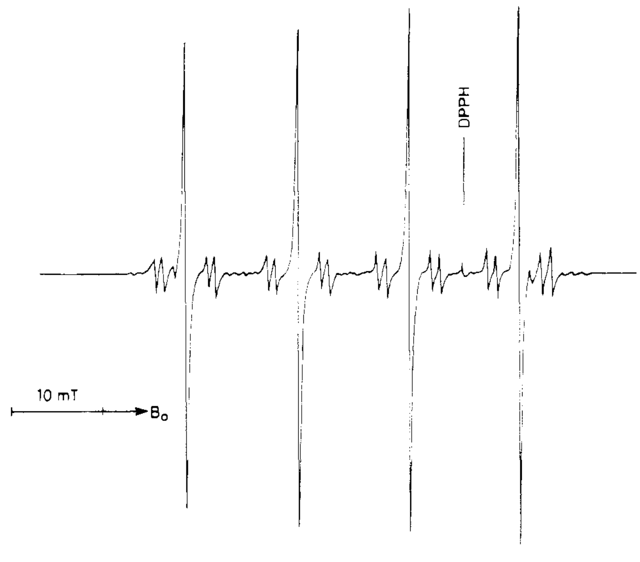

Figure 1. Typical single-crystal EPR spectrum of $(n\text{-Bu}_4\text{N})_2[^{63}\text{Cu/Ni(dsit)}_2]$ for $\mathbf{B}_0$ lying in the *ac* plane. Both $[^{63}\text{Cu(dsit)}_2]^{2-}$ sites coincide, and the ^{77}Se satellites of two pairs of Se nuclei are clearly seen.

netically nonequivalent $[^{63}\text{Cu(dsit)}_2]^{2-}$ anions for a general direction of the magnetic field $\mathbf{B}_0$. A plane can be easily found in which the signals of both sites coincide. For the $P2_1/c$ space group this situation is expected when the $\mathbf{B}_0$ field lies in the *ac* plane.

In the spectra, each ^{63}Cu line is flanked symmetrically by two pairs of ^{77}Se ligand hfs satellites due to the interaction of the unpaired electron with the nuclear spin of the ^{77}Se isotope. The intensity of the satellite lines is approximately 8% of that of the ^{63}Cu hfs signal. These satellites arise from complex molecules containing one ^{77}Se atom. With higher amplification, satellites due to molecules with two ^{77}Se atoms could be observed also. Because these did not yield additional information, they have been ignored. A representative spectrum is shown in Figure 1.

The EPR spectra were analyzed in terms of the spin-Hamiltonian

$$H_{\text{sp}} = \mu_{\text{B}}\mathbf{B}_0\cdot\mathbf{g}\cdot\mathbf{S} + \mathbf{S}\cdot\mathbf{A}^{\text{Cu}}\cdot\mathbf{I}^{\text{Cu}} + \mathbf{I}^{\text{Cu}}\cdot\mathbf{P}^{\text{Cu}}\cdot\mathbf{I}^{\text{Cu}} - g_{\text{N}}\mu_{\text{N}}\mathbf{B}_0\cdot\mathbf{I}^{\text{Cu}} + \sum_{i=1}^{2}(\mathbf{S}\cdot\mathbf{A}^{\text{Se}_i}\cdot\mathbf{I}^{\text{Se}_i} - g_{\text{N}}\mu_{\text{N}}\mathbf{B}_0\cdot\mathbf{I}^{\text{Se}_i}) \quad (1)$$

The last term in (1) contains the ^{77}Se ligand hfs interaction; all symbols have their usual meaning.

The analysis of the angular dependence showed a complicated situation for the directions of the principle axes of the g tensor, the ^{63}Cu hfs tensor $\mathbf{A}^{\text{Cu}}$ and the ^{63}Cu nuclear quadrupole tensor $\mathbf{P}^{\text{Cu}}$: Except for the smallest components of g and $\mathbf{A}^{\text{Cu}}$, g_3 and A_3^{Cu}, which nearly point in the same direction (the bisector of the Se$_1$–Cu–Se$_2$ angle), none of the other principal axes of g and $\mathbf{P}^{\text{Cu}}$ coincide with a principal axis of $\mathbf{A}^{\text{Cu}}$. The g tensor components g_1 and g_2 are rotated by 20° from those of $\mathbf{A}^{\text{Cu}}$.

The hfs tensors of both pairs of Se atoms are slightly different from each other. The angle between the maximum components $A_1^{\text{Se}_1}$ and $A_1^{\text{Se}_2}$ is 93°, which should be almost identical with the crystallographic Se$_1$–Ni–Se$_2$ angle if the incorporated Cu complex accepts the structure of the host complex. This follows from symmetry arguments: for an almost planar Cu complex, the maximum ligand hfs components are expected to lie along the donor atom-metal bond.[11-13] For $[\text{Ni(dsit)}_2]^{2-}$, the corresponding Se$_1$–Ni–Se$_2$ angle was determined to be 93.3°.[16] Furthermore, the observation of only two different ^{77}Se tensors is in agreement with presence of an inversion center for the incorporated Cu complex too.

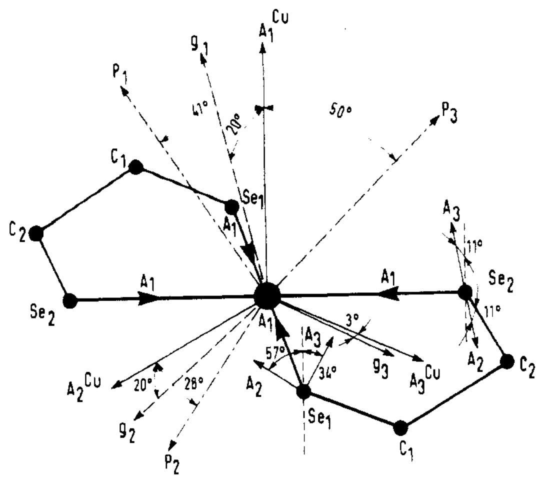

Figure 2. Directions of the principal axes of g, $\mathbf{A}^{\text{Cu}}$, $\mathbf{P}^{\text{Cu}}$, and $\mathbf{A}^{\text{Se}_{1(2)}}$ in the molecular frame.

Table I. EPR Parameters of $(n\text{-Bu}_4\text{N})_2$ $[^{63}\text{Cu/Ni(dsit)}_2]$ and $(n\text{-Bu}_4\text{N})_2[^{63}\text{Cu/Ni(dmit)}_2$[a]

		$[\text{Cu(dsit)}_2]^{2-}$	$[\text{Cu(dmit)}_2]^{2-}$
g	g_1	2.105	2.101
	g_2	2.067	2.027
	g_3	2.018	2.025
	g_{av}	2.063	2.051
$\mathbf{A}^{\text{Cu}}$	A_1	−151.3	−158.7
	A_2	−56.3	−39.6
	A_3	−43.7	−36.4
	A_{av}	−83.8	−78.2
$\mathbf{P}^{\text{Cu}}$	P_1	2.0	*b*
	P_2	−0.3	
	P_3	−1.7	
$\mathbf{A}^{\text{S(e)}_1}$	A_1	108.7	22.4
	A_2	46.2	9.9
	A_3	39.7	10.5
	A_{av}	64.9	14.3
$\mathbf{A}^{\text{S(e)}_2}$	A_1	101.3	21.2
	A_2	43.9	10.0
	A_3	35.8	10.5
	A_{av}	60.3	13.9

[a] Hyperfine couplings in 10^{-4} cm^{-1}. Experimental errors for $[\text{Cu(dsit)}_2]^{2-}$: g_i, ±0.002; $A_i^{\text{Cu,Se}}$, ±1.0; P_i^{Cu}, ±1.0). [b] Not determined.

Table II. Angles (deg) between Principal Axes of $\mathbf{A}^{\text{Cu}}$ and Principal Axes of g, $\mathbf{A}^{\text{Se}}$, and $\mathbf{P}^{\text{Cu}}$

		A_1^{Cu}	A_2^{Cu}	A_3^{Cu}
g	g_1	20	70	90
	g_2	110	20	87
	g_3	89	93	3
$\mathbf{A}^{\text{Se}_1}$	A_1	90	136	135
	A_2	34	113	67
	A_3	57	55	53
$\mathbf{A}^{\text{Se}_2}$	A_1	94	43	132
	A_2	98	48	42
	A_3	11	82	87
$\mathbf{P}^{\text{Cu}}$	P_1	41	77	127
	P_2	85	28	63
	P_3	50	114	50

From the directions of the maximum components of the ^{77}Se hfs tensors, the orientations of all other tensor components in the molecular frame can now be determined. They are sketched in Figure 2. The maximum component of $\mathbf{A}^{\text{Cu}}$, A_1^{Cu}, is found to be perpendicular to the plane spanned by $A_1^{\text{Se}_1}$ and $A_1^{\text{Se}_2}$, which is also in agreement with the assumption of a planar complex molecule. The principal values of the various tensors are listed in Table I; in addition, the corresponding values for $[\text{Cu(dmit)}_2]^{2-}$ are given for comparison. The orientations of the principal axes of g, $\mathbf{A}^{\text{Se}_1}$, $\mathbf{A}^{\text{Se}_2}$, and $\mathbf{P}^{\text{Cu}}$ with respect to the principal axes of $\mathbf{A}^{\text{Cu}}$ are given in Table II.

The spin-Hamiltonian parameters derived are used to calculate the powder EPR spectrum of $(n\text{-Bu}_4\text{N})_2[^{63}\text{Cu/Ni(dsit)}_2]$. The experimentally obtained spectrum and the simulated spectrum are shown in Figure 3. All features of the experimental spectrum are well reproduced. It should be noted that, for a spin system with noncoinciding principal axes of g and A, line shifts are expected which result in a more or less pronounced disturbance

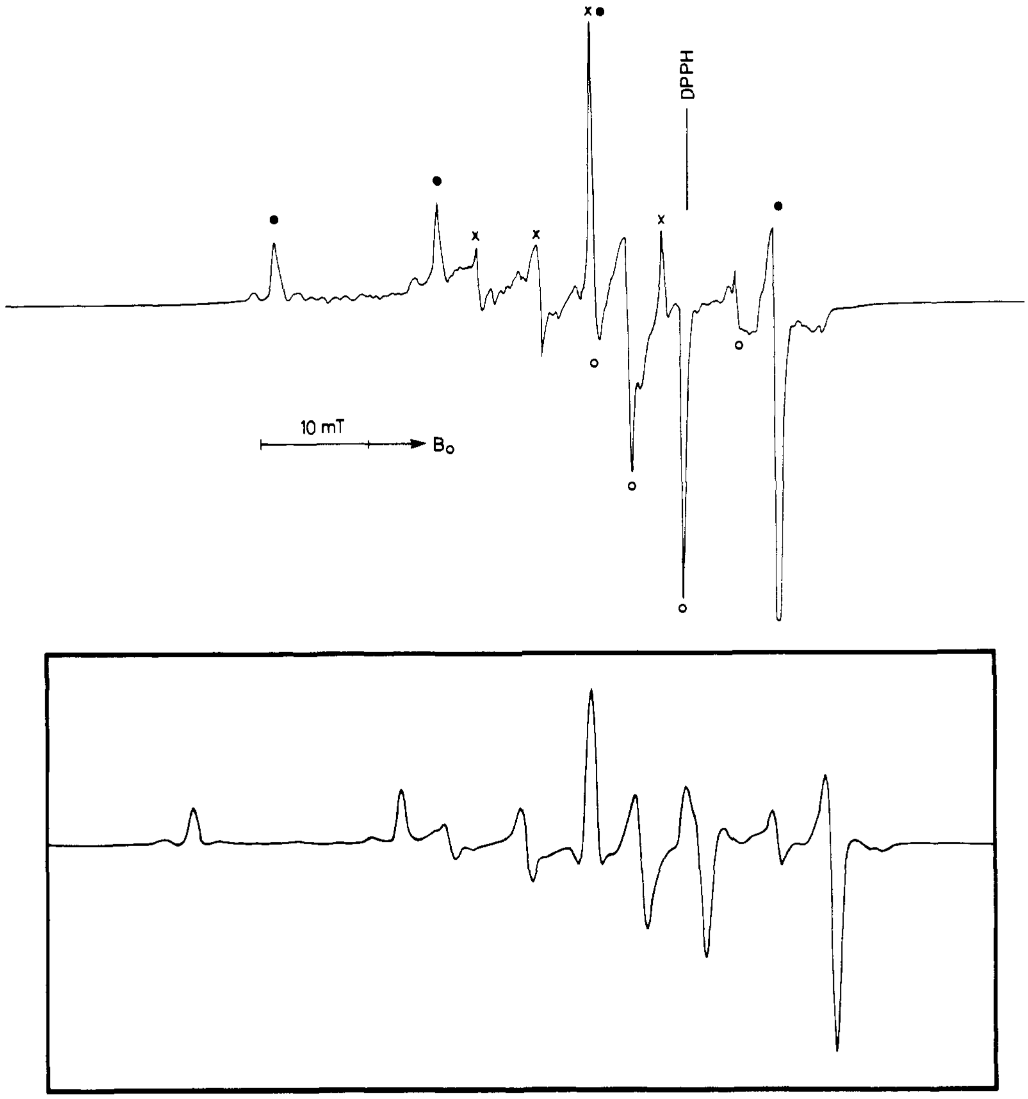

Figure 3. Experimental (a, top) and simulated (b, bottom) powder EPR spectrum of $(n\text{-}Bu_4N)_2[^{63}Cu/Ni(dsit)_2]$. In part a the ^{63}Cu hfs lines belonging together are marked by ○, ●, and ×.

of the line equidistance within the hfs multiplets.[11,12] In such cases it is not expected that correct values can be derived from the powder spectrum. For the system under study, without knowledge of the single-crystal data, the following parameters are obtained: $g_1 = 2.100$, $g_2 = 2.075$, $g_3 = 2.019$, $A_1^{Cu} = 152 \times 10^{-4}$ cm^{-1}, $A_2^{Cu} = 53 \times 10^{-4}$ cm^{-1}, and $A_3^{Cu} = 42 \times 10^{-4}$ cm^{-1} ($g_i \pm 0.002$, $A_i^{Cu} \pm 2 \times 10^{-4}$ cm^{-1}). As expected, deviations outside the error limits occur for the principal values g_1, g_2, A_1^{Cu}, and A_2^{Cu}.

As found for copper(II) dithiolene complexes,[17] the EPR parameters of the title compound suggest a MO for the unpaired electron that can be written as

$$\Psi_{B_{1g}} = \alpha|d_{xy}\rangle - (\alpha^{Se_1}/2^{1/2})(-\sigma^1 + \sigma^3) - (\alpha^{Se_2}/2^{1/2})(-\sigma^2 + \sigma^4) \tag{2}$$

where

$$\sigma^i = (1 - n^2)^{1/2}s^i \pm np^i \tag{3}$$

The MO coefficient α can be estimated from the values obtained for the $\mathbf{A}^{Cu}$ and **g** tensor components and the commonly used formulas given by McGarvey.[18] From the relations $A_{av}^{Se}(\exp) = (A_{av}^{Se}(\text{calc}))C_s^2$ and $A_{dip}^{Se}(\exp) = (A_{dip}^{Se}(\text{calc}))C_p^2$, the spin densities in the Se 4s and 4p orbitals, C_s^2 and C_p^2, can be derived. The MO coefficients α^{Se_1} and α^{Se_2} and the hybridization degree n can now be estimated by means of the equations $(\alpha^{Se})^2 = 2(C_s^2 + C_p^2)$ and $n^2 = 2C_p^2/(\alpha^{Se})^2$. The following values are obtained (using $A_{av}^{Se}(\text{calc}) = (8\pi/3)g_e\mu_B g_{Se}\mu_n|\Psi_{4s}(0)|^2 = 4492.4 \times 10^{-4}$ cm^{-1} and $A_{dip}^{Se}(\text{calc}) = (2/5)g_e\mu_B g_{Se}\mu_n\langle r^{-3}\rangle = 125.4 \times 10^{-4}$ cm^{-1} [19]): $\alpha^2 = 0.43$, $(\alpha_1^{Se})^2 = 0.38$, $(\alpha_2^{Se})^2 = 0.35$, $(n(Se_1))^2 = 0.92$, and $(n(Se_2))^2 = 0.93$. Compared with the corresponding values evaluated for $[Cu(dmit)_2]^{2-}$ ($\alpha^2 = 0.56$, $(\alpha_1^S)^2 = 0.31$, $(\alpha_2^S)^2 = 0.29$, $(n(S_1))^2 = (n(S_2))^2 = 0.95$) for the diselenole complex, the delocalization of the unpaired electron is noticeably larger. The n^2 values estimated for $[Cu(dmit)_2]^{2-}$ are obviously too large due to the greater relative error of the ^{33}S spectra analysis.

It is interesting to compare the ^{77}Se tensors with those earlier reported for the bis(dialkyldiselenocarbamato)copper(II) complexes, $Cu(R_2dsc)_2$:[11-13] A_{av}^{Se} values of (45–49) × 10^{-4} cm^{-1} and A_{dip}^{Se} values of (28–30) × 10^{-4} cm^{-1} have been measured. For $[Cu(dsit)_2]^{2-}$ the A_{av}^{Se} values (60.3×10^{-4} and 64.9×10^{-4} cm^{-1}) are considerably larger; however, the A_{dip}^{Se} values (20.5×10^{-4} and 21.9×10^{-4} cm^{-1}) are noticeably smaller. This clearly reflects a stronger hybridization of the Se 4s and 4p orbitals and correponds well to the enlarged C–Se–Cu angle in the five-membered chelate rings in $[Cu(dsit)_2]^{2-}$. For $[Ni(dsit)_2]^{2-}$, the two C–Se–Ni angles were found to be 101.2 and 102.1°.[16]

A comment must be made concerning the g tensor. A comparison with that obtained for $[Cu(dmit)_2]^{2-}$ shows some striking differences: (i) In contrast to that found for $[Cu(dmit)_2]^{2-}$, the g tensor found for $[Cu(dsit)_2]^{2-}$ has pronounced rhombic symmetry. (ii) The principal axes of **g** and $\mathbf{A}^{Cu}$ do not coincide. (iii)

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A noticeable increase (by 0.012) in the isotropic part g_{av} is observed for the diselenolene complex. A similar situation has been found for the bis(dialkyldichalcogenocarbamato)copper(II) complexes $Cu(R_2dsc)_2$ and $Cu(R_2dtc)_2$, which represent another $CuS_4/CuSe_4$ couple. Also in this case the **g** tensor becomes more rhombic and its principal axes do not coincide with those of A^{Cu} on going from the CuS_4 to the $CuSe_4$ complex. According to detailed MO calculations[13,20] made on these systems, the increased **g** anisotropy in the coordination plane (see Table I) is mainly due to the large spin-orbit coupling of the Se donor atoms (the spin-orbit coupling constant of Se is λ_{Se} = 1690 cm^{-1}, which is larger than that of Cu by a factor of 2), giving rise to enhanced ligand orbital contributions of different weight (mainly Se $4p_z$ orbits of an antibonding state) to the corresponding **g** components. Of course delocalization reduces the effect of the Cu spin-orbit contribution to the **g** tensor, but apparently the spin-orbit contribution of the Se atoms more than compensate for this. However, for the $Cu(R_2dsc)_2$ complexes, instead of an increase, a decrease of g_{av} by about 0.025 was found. Since the covalency of the Cu-Se bonds in $[Cu(dsit)_2]^{2-}$ comes close to that observed for the copper diselenocarbamates, this can only be understood if for $[Cu(dsit)_2]^{2-}$ the d-d excitation energies of the MO's that contribute to the principal **g** values are smaller than those of $Cu(R_2dsc)_2$. Unfortunately, in the electronic spectrum of $[Cu(dsit)_2]^{2-}$, an unambiguous assignment of the transitions observed cannot be made, and detailed MO calculations, which could clarify the situation, require also the knowledge of exact X-ray structural data for the Cu complex, which are not available.

The noncoincidence of the principal axes can only be observed if the symmetry of the complex is lower than rhombic symmetry. Furthermore, MO calculations on diselenocarbamates have shown that also the 4d Se ortibals have to be included in the calculations to account for the noncoincidence of the **g** and **A** tensors.[13,20]

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Synthesis and Characterization of Alkali-Metal Titanium Alkoxide Compounds $MTi(O\text{-}i\text{-}Pr)_5$ (M = Li, Na, K): Single-Crystal X-ray Diffraction Structure of $[LiTi(O\text{-}i\text{-}Pr)_5]_2$

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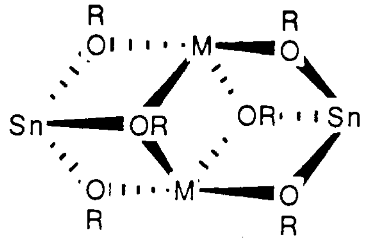
The series $[MTi(O\text{-}i\text{-}Pr)_5]$, M = Li, Na, or K, has been prepared by the reaction of MO-*i*-Pr with $Ti(O\text{-}i\text{-}Pr)_4$. A single-crystal X-ray diffraction study revealed that $[LiTi(O\text{-}i\text{-}Pr)_5]$ crystallizes from toluene at -30 °C in the monoclinic space group $P2_1/n$, with unit cell dimensions a = 11.440 (8) Å, b = 16.396 (13) Å, c = 11.838 (8) Å, β = 92.59 (5)°, and Z = 4, as a dimer containing two approximately trigonal-bipyramidal titanium centers linked by lithium bridges. In benzene solution, all three compounds are dimeric, as revealed by cryoscopic molecular weight determination, and all three undergo an alkoxide ligand exchange process that is rapid on the ^{1}H NMR time scale at room temperature. The positions of ν(M-O) are assigned based on the low-energy shifts observed upon deuteriation of the isopropoxide ligands.

Introduction

The use of metal alkoxides as molecular precursors for electronic and ceramic materials is an area of intense current interest and has recently been reviewed.[1] The sol-gel technique for hydrolytic condensation has been used for many years as a low-temperature method for conversion of metal alkoxides to metal oxides.[2] For example, hydrolysis of mixtures of $[Sr(O\text{-}i\text{-}Pr)_2]$ with $[Ti(O\text{-}i\text{-}Pr)_4]$ or $[Zr(O\text{-}i\text{-}Pr)_4]$, followed by calcination at 350 °C, resulted in formation of crystalline perovskite phases, $SrTiO_3$ and $SrZrO_3$.[3] Another advantage of the sol-gel process lies in control over homogeneity on the molecular level. Although there are many examples of the use of this technique for the synthesis of ternary metal oxide phases[1,2] and many examples of mixed-metal alkoxide compounds in the literature,[4] there is very little structure information available. Perhaps the best characterized series of mixed-metal alkoxides is $MSn(O\text{-}t\text{-}Bu)_3$ in which M has been systematically varied (M = Li, Na, K, Rb, Cs, Tl), revealing some interesting trends.[5] Whereas M = Li and Na derivatives are dimeric, with a common $Sn_6O_6M_2$ cage as a structural feature, M = K, Rb, and Cs derivatives exist as one-dimensional infinite polymers with a common SnO_3M cage, and the M = Tl derivative exists as a monomer in the solid state. These trends have been examined in a recent review article.[6] A notable feature of the structure of the $LiMSn(O\text{-}t\text{-}Bu)_3$ (M = Li, Na) analogues is the coordination environment of the alkali-metal ions,



which could be described as distorted octahedral with two cis

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