The last part of the spectrum originates from the $[Ni(dmit)_2]^-$ and $(tmpd)_2^+$ species and merely gives an intense single absorption at $g = 2.01$. No hyperfine structure due to the methyl groups of the dimer is found. In Figure 4, all absorptions according to the fitted parameters are indicated and only minor deviations from the recorded spectrum can be observed.

Susceptibility Measurements. The magnetic susceptibility of $[tmpd]_3[Ni(dmit)_2]$ shows paramagnetic behavior, which follows a Curie law with an effective magnetic moment of only 0.7 μ_B per unit cell (80–300 K). This very low magnetic moment clearly indicates that, in $[tmpd]_3[Ni(dmit)_2]$, Ni is not in its Ni(III) oxidation state, as this would give rise to a magnetic moment of at least 1.7 μ_B. However, the low moment can be explained by the distribution of Ni(II) and Ni(III) units.

From the analysis carried out in the previous sections it follows that only roughly 25% of the Ni atoms possess a charge of 1+ and thus carry a spin; the Ni^{2+} atoms are in the low-spin state and consequently do not have a moment. The same accounts for the $(tmpd)_2$ dimers, as only the singly charged species carry an unpaired spin. Using these numbers for the spin-carrying species and ignoring any interactions, a magnetic moment of 0.8 μ_B per unit cell is obtained, close to the observed value of 0.7 μ_B. Due to the fact that the susceptibility is completely dominated by the spins on $(tmpd)_2^{2+}$ and $[Ni(dmit)_2]^-$, no effect of the triplet state of the $(tmpd)_2^{2+}$ dimer could be observed.

Concluding Remarks

To the best of our knowledge $[tmpd]_3[Ni(dmit)_2]$ is the first $[Ni(dmit)_2]$-based compound containing a nitrogen-rich radical cation known sofar. Although the starting material in the electrochemical synthesis was a Ni(III) complex, the charge-transfer salt probably contains both Ni(II) and Ni(III) species. This mixed valence, however, is static, at least on the time scale of EPR spectroscopy, as is shown by the EPR spectrum containing both $(tmpd)_2^+$ and $(tmpd)_2^{2+}$ parts, the latter characterized by its triplet state. When $[tmpd]_3[Ni(dmit)_2]$ and $[ttf][Ni(dmit)_2]_2$, a metallic conductor, are compared, the enormous difference in conductivity may be explained from the fact that in the ttf compound large intermolecular overlaps exist, which are absent in $[tmpd]_3[Ni(dmit)_2]$. The angle between the planes of the $Ni(dmit)_2$ and tmpd units (70°) prevents conductivity via the cation.[17]

Acknowledgment. We thank Mr. S. Gorter for collecting diffraction data and Dr. H. B. Brom for valuable discussions on the EPR spectrum. This work was sponsored by the Leiden Materials Research Center (Werkgroep Fundamenteel Materialen Onderzoek).

Registry No. tmpd, 100-22-1; $[Bu_4N][Ni(dmit)_2]$, 68401-88-7.

Supplementary Material Available: Tables of crystallographic details, anisotropic thermal parameters, hydrogen positions and thermal parameters, bond distances and angles involving hydrogen atoms, and equations of least-squares planes and deviations (10 pages); a table of calculated and observed structure factors (14 pages). Ordering information is given on any current masthead page.

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Comparative Study of NS_2 Ligands, *S*-Alkyl vs *S*-Aryl. Molecular Structure of [2,6-Bis(((2-(methoxycarbonyl)phenyl)thio)methyl)pyridine]dichlorocopper(II)

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Three new NS_2 aza–dithia *S*-aryl ligands have been synthesized and their Cu(II) and Cu(I) complexes reported. The ligand donor properties of these ligands are compared with similar NS_2 *S*-alkyl molecules. The NS_2 *S*-aryl ligands are softer and display a larger π-acid character than the corresponding NS_2 *S*-alkyl compounds. The molecular structure of [2,6-Bis(((2-methoxycarbonyl)phenyl)thio)methyl)pyridine]dichlorocopper(II) has been solved by X-ray diffraction methods: $C_{23}H_{21}Cl_2CuNO_4S_2$, monoclinic, space group $P2_1/c$, $a = 20.138$ (4) Å, $b = 8.173$ (1) Å, $c = 15.533$ (3) Å, $\beta = 111.20$ (2)°, $V = 2384$ (1) Å^3, $Z = 4$, $D_c = 1.600$ g·cm^{-3}.

Introduction

Relatively little work has been carried out on the NS_2 aza–thia compounds either as podand[1-3] or as macrocyclic[2,4-12] ligands. All these compounds contain the group 2,6-bis(thiomethyl)pyridine, which is the source of the NS_2 coordinating moiety. Recently, the macrocycle $[9]NS_2$ (7-aza-1,4-dithiacyclononane) has been reported by two independent groups (Ag(I) complex,[13] Ni(II) complex[14]). All these ligands contain both the hard N-donor and soft S-donor atoms. Interest in such mixed-donor ligands stems from metal ion selectivity and from the possible presence of such coordination environments around metal centers in methanogenic bacterial enzymes.[15,16]

Recent studies in our group have been shown that there is little discrimination of Cu(II) vs Ni or Co(II) ($K^{Pot}_{Cu,Ni} = 0.1$) in the all-solid-state electrode based on PVC, a mediating solvent (tris(2-ethylhexyl) phosphate), and the NS_2 sensor MO1[10] (Figure 1). This result stimulated us to study similar NS_2 ligands but

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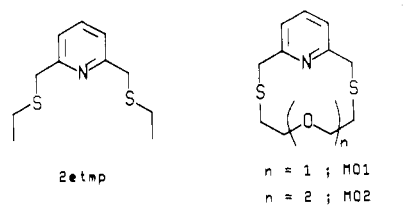

Figure 1. Schematic drawings for the 2etmp, MO1, and MO2 ligand molecules.

having the sulfur elements connected to one aryl group. The existence of this aryl group should modify the coordinating characteristics of this new type of NS_2 ligand and, expectedly, the discrimination ability. The fact that never previously had such type of NS_2(*S*-aryl) ligand been studied prompted us to study the coordinating behavior and the physical characteristics of the resulting complexes.

In this paper we report on the synthesis of this type of NS_2(*S*-aryl) ligand, their reactivity toward Cu(II)/Cu(I) metal ions, and their comparison with the analogue complexes of NS_2(*S*-alkyl).

Experimental Section

All ligands were synthesized under a dinitrogen atmosphere unless otherwise stated. Dehydrated and deoxygenated solvents were used in the ligand syntheses. Methanol was dehydrated using Mg. Solvents were placed under vacuum to eliminate dissolved oxygen. In all cases this treatment was sufficient to perform the reaction. 2,6-Bis(bromomethyl)pyridine,[17] [(2etmp)$CuCl_2$],[2] [(MO1)$CuCl_2$], and ([MO2)$CuCl_2$][10] were prepared according to reported procedures. Thiophenol and *p*-chlorothiophenol were commercially available (Aldrich) and used as received.

Microanalyses (C, H, N) were performed in our analytical laboratory on a Perkin-Elmer 240-B instrument. Proton NMR spectra were recorded on a Bruker 400 MHz AM instrument. Electronic spectra were recorded on a Kontron Uvicon-860 spectrophotometer, and infrared spectra, on an FT-IR Perkin-Elmer 1740 spectrophotometer with KBr pellets.

Cyclic voltammetric measurements were performed under a dry dinitrogen atmosphere on 1 mM solutions of the complexes in dry nitromethane that contained 0.1 M Et_4NPF_6 as a supporting electrolyte at a rate 20–100 mV s^{-1}. A glassy-carbon button working electrode and platinum-wire counter electrode were used with a NaCl-saturated calomel electrode (SSCE) as reference. A Dacfamov 05.10 CNRS-Microtec apparatus, equipped with an Apple IIe microcomputer, was used.

EPR spectra were obtained with a Varian E-109 instrument, operating at the X-band frequency (ca. 9.5 GHz). The free-radical DPPH (g = 2.0036) was used as a field marker in all cases. Spectra were taken of nitromethane solutions at room temperature.

2,6-Bis((phenylthio)methyl)pyridine (L1). To a stirred solution of sodium metal (1.21 g, 52 mmol) in methanol (30 cm^3) was added thiophenol (5.81 g, 52 mmol), and the mixture was stirred for a further 10 min. The solution was then added to another one of 2,6-bis(bromomethyl)pyridine (7 g, 26.4 mmol) in methanol (30 cm^3). After 3 h under stirring at 0 °C, the solvent was eliminated under reduced pressure. The resulting yellow residue was extracted with diethyl ether (100 cm^3), and the organic layer was washed twice with aqueous 1 M NaOH (50 cm^3) and twice with water (50 cm^3), dried ($MgSO_4$), and vacuum evaporated to afford impurified L1 as a yellow oil (7.38 g). Purification of this product was achieved by formation of the copper(II) chloride complex and further destruction with KCN. The yellow oil obtained, dissolved in methanol (30 cm^3), was added to a solution of $CuCl_2{\cdot}2H_2O$ (3.9 g, 22.8 mmol) in methanol (30 cm^3). A brown precipitate appeared, which was filtered off, washed with diethyl ether (20 cm^3), vacuum dried, and redissolved in hot methanol (200 cm^3). To this solution was added, dropwise, another one of KCN (3.32 g, 51 mmol) in methanol (50 cm^3). The mixture turn gradually colorless, and a white precipitate appeared. After completion of addition, the mixture was stirred for 1 h and then filtered and the solid (CuCN and KCl) rejected. The clear solution was evaporated until an orange oil appeared. The oil was dissolved in diethyl ether (100 cm^3), washed twice with aqueous 1 M NaOH (50 cm^3) and twice with water (50 cm^3), dried ($MgSO_4$), and vacuum evaporated. The yellow oil obtained was recrystallized with light petroleum ether (40–70 °C) to obtain L1 as a white microcrystalline solid. Yield: 21% (1.75 g). ^1H NMR (acetone-d_6): δ 4.23 (4 H, s, py-CH_2-S) and 7.15–7.49 (13 H, m, aromatics). Anal. Calcd for $C_{19}H_{17}NS_2$: C, 70.55; H, 5.30; N, 4.33. Found: C, 70.53; H, 5.45; N, 4.33.

2,6-Bis(((4-Chlorophenyl)thio)methyl)pyridine (L2). This product was prepared and purified analogously to the method described for L1, using 4-chlorothiophenol (7.69 g, 52 mmol) as starting material. Yield: 13% (1.28 g). ^1H NMR (acetone-d_6): δ 4.29 (4 H, s, py-CH_2-S) and 7.27–7.65 (11 H, m, aromatics). Anal. Calcd for $C_{19}H_{15}NS_2Cl_2$: C, 58.16; H, 3.85; N, 3.57. Found: C, 58.13; H, 3.76; N, 3.45.

2,6-Bis(((2-(methoxycarbonyl)phenyl)thio)methyl)pyridine (L3). To a stirred solution of sodium metal (0.93 g, 40 mmol) in methanol (40 cm^3) was added thiosalicyl methyl ester (2.90 g, 40 mmol), and the mixture was stirred for a further 10 min. The solution was then added to another one of 2,6-bis(bromomethyl)pyridine (5.30 g, 20 mmol) in methanol (40 cm^3). After addition, a white precipitate appeared. The mixture was heated at 30–35 °C under reflux for 30 min and then cooled at room temperature. The precipitate was filtered off, washed with methanol, vacuum dried, and recrystallized with 1,2-dimethoxyethane to afford L3 as a white microcrystalline product. Yield: 42% (70.38 g). IR: $\tilde{\nu}$(C=O) 1700 cm^{-1}. ^1H NMR (acetone-d_6): δ 3.91 (6 H, s, CH_3-OOC), 4.31 (4 H, s, py-CH_2-S), and 7.13–7.97 (11 H, m, aromatics). Anal. Calcd for $C_{23}H_{21}NO_4S_2$: C, 62.85; H, 4.82; N, 3.19. Found: C, 62.33; H, 4.84; N, 3.17.

Copper(II) Complexes. All the copper(II) chloride complexes were prepared by the same procedure.

[(L1)$CuCl_2$]. The ligand L1 (0.20 g, 0.62 mmol) dissolved in methanol (2 cm^3) was added to a solution of $CuCl_2{\cdot}2H_2O$ (0.11 g, 0.62 mmol) in methanol (2 cm^3). A solid was obtained in microcrystalline form, which was filtered off, washed with methanol (2 cm^3) and diethyl ether (5 cm^3), and vacuum dried. Color: yellow-brown. Yield: 78% (0.22 g). Anal. Calcd for $C_{19}H_{17}NS_2Cl_2Cu$: C, 49.83; H, 3.74; N, 3.06. Found: C, 49.67; H, 3.72; N, 3.02.

[(L2)$CuCl_2$]. Color: red-brown. Yield: 77% (0.24 g). Anal. Calcd for $C_{19}H_{15}NS_2Cl_4Cu$: C, 43.32; H, 2.87; N, 2.66. Found: C, 43.12; H, 2.82; N, 2.61.

[(L3)$CuCl_2$]. Color: red. Yield: 38% (0.14 g). IR: $\tilde{\nu}$(C=O) 1708 cm^{-1}. Anal. Calcd for $C_{23}H_{21}NO_4S_2Cl_2Cu$: C, 48.13; H, 3.69; N, 2.44. Found: C, 48.26; H, 3.68; N, 2.43.

The copper(II) perchlorate complexes of ligands L1 and L2 were prepared as follows.

[(L1)Cu(ClO_4)$_2$]·H_2O. The ligand L1 (0.20 g, 0.62 mmol) dissolved in ethyl acetate (2 cm^3) was added to a solution of $Cu(ClO_4)_2{\cdot}6H_2O$ (0.24 g, 0.62 mmol) in ethyl acetate (2 cm^3). A brown oil was obtained, which was solidified by addition of diethyl ether (0.5 cm^3). The solid obtained was filtered off, washed and diethyl ether (2 cm^3), and vacuum dried. Color: violet. Yield: 44% (0.16 g). Anal. Calcd for $C_{19}H_{19}NO_9S_2Cl_2Cu$: C, 37.79; H, 3.17; N, 2.32. Found: C, 37.01; H, 3.35; N, 2.35.

[(L2)Cu(ClO_4)$_2$]·H_2O. Color: violet. Yield: 54% (0.22 g). Anal. Calcd for $C_{19}H_{17}NO_9S_2Cl_4Cu$: C, 33.92; H, 2.55; N, 2.08. Found: C, 33.05; H, 2.55; N, 2.01.

[(L3)Cu(ClO_4)$_2$]. The ligand L3 (0.27 g, 0.62 mmol) dissolved in ethyl acetate (2 cm^3) was added to a solution of $Cu(ClO_4)_2{\cdot}6H_2O$ (0.24 g, 0.62 mmol) in ethyl acetate (2 cm^3). A solid was obtained in microcrystalline form, which was filtered off, washed with methanol (2 cm^3) and diethyl ether (5 cm^3), and vacuum dried. Color: violet. Yield: 73% (0.31 g). IR: $\tilde{\nu}$(C=O) 1700 cm^{-1}. Anal. Calcd for $C_{23}H_{21}NO_{12}S_2Cl_2Cu$: C, 39.35; H, 3.02; N, 2.00. Found: C, 40.86; H, 3.36; N, 2.09.

Copper(I) Complexes. The copper(I) cyanide complexes were prepared as follows.

[(L1)Cu(CN)]. To a mixture of [(L1)$CuCl_2$] (0.28 g, 0.62 mmol) in methanol (50 cm^3) was added, dropwise, a 0.05 M KCN methanolic solution until the complex was dissolved and the solution turn colorless. At this point, the solution was allowed to stand overnight. A yellow solid appeared, which was filtered off, washed with diethyl ether (2 cm^3), and vacuum dried. Yield: 31% (0.08 g). IR: $\tilde{\nu}$(CN) 2119 cm^{-1}. Anal. Calcd for $C_{20}H_{17}N_2S_2Cu$: C, 58.16; H, 4.15; N, 6.78. Found: C, 57.80; H, 4.10; N, 6.61.

[(L2)Cu(CN)]. Yield: 30% (0.089 g). IR: $\tilde{\nu}$(CN) 2120 cm^{-1}. Anal. Calcd for $C_{20}H_{15}N_2S_2Cl_2Cu$: C, 49.86; H, 3.14; N, 5.81. Found: C, 49.74; H, 3.07; N, 5.73.

X-ray Structure Determination of [2,6-Bis(((2-(methoxycarbonyl)phenyl)thio)methyl)pyridine]dichlorocopper(II), [(L3)$CuCl_2$]. Red single crystals of this stoichiometry were obtained by slow evaporation of a methanolic solution. The unit cell parameters were determined by least-squares refinement of 25 carefully centered high-angle reflections measured on a Syntex P2$_1$ diffractometer. Crystal data are presented

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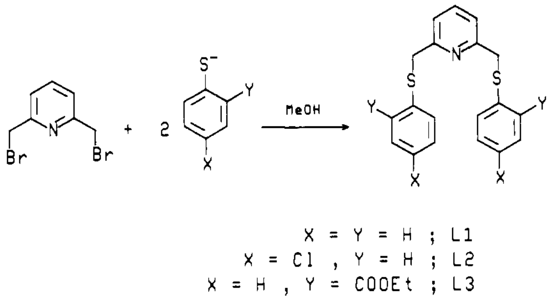
Table I. Crystallographic Data for [2,6-Bis((2-(methoxycarbonyl)phenyl)thio)methyl)pyridine]dichlorocopper(II)

chem formula: $C_{23}H_{21}NO_4S_2Cl_2Cu$
$a = 20.138\ (4)$ Å
$b = 8.173\ (1)$ Å
$c = 15.533\ (3)$ Å
$\beta = 111.20\ (2)°$
$V = 2384\ (1)$ Å^3
$Z = 4$
$T = 22$ °C
fw = 573.5
space group: monoclinic, $P2_1/c$
$\lambda = 0.71069$ Å
$\rho_{calcd} = 1.600$ g cm^{-3}
$\mu = 13.4$ cm^{-1}
transm coeff = 0.958–1.000
$R(F_o) = 0.041$
$R_w(F_o) = 0.032$

Scheme I



Scheme II

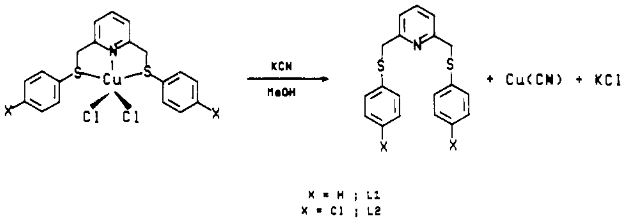


Table II. Non-Hydrogen Coordinates and Isotropic Thermal Parameters with Their Estimated Standard Deviations (Esd's) for [(L3)$CuCl_2$]

atom	*x/a*	*y/b*	*z/c*
Cu(1)	0.24133 (3)	0.18770 (7)	0.21453 (4)
S(1)	0.17922 (6)	−0.3608 (1)	0.08480 (8)
S(2)	0.30606 (6)	0.0376 (2)	0.31053 (8)
Cl(1)	0.14971 (6)	0.1028 (2)	0.25316 (8)
Cl(2)	0.33129 (6)	0.3657 (1)	0.24359 (9)
O(1)	0.0208 (2)	0.5109 (4)	0.2003 (2)
O(2)	0.1319 (1)	0.5185 (4)	0.2006 (2)
O(3)	0.4557 (2)	0.3099 (4)	0.4940 (2)
O(4)	0.3524 (1)	0.1745 (4)	0.4512 (2)
N(1)	0.2440 (2)	0.0259 (4)	0.1055 (2)
C(1)	0.0422 (3)	0.6249 (6)	0.2766 (3)
C(2)	0.0713 (2)	0.4695 (5)	0.1675 (3)
C(3)	0.0430 (2)	0.3611 (5)	0.0853 (3)
C(4)	−0.0299 (2)	0.3215 (6)	0.0502 (3)
C(5)	−0.0564 (2)	0.2213 (6)	−0.0259 (3)
C(6)	−0.0125 (2)	0.1609 (6)	−0.0681 (3)
C(7)	0.0598 (2)	0.2016 (6)	−0.0350 (3)
C(8)	0.0878 (2)	0.3025 (5)	0.0415 (3)
C(9)	0.2157 (2)	0.2648 (6)	0.0065 (3)
C(10)	0.2291 (2)	0.0828 (6)	0.0197 (3)
C(11)	0.2288 (2)	−0.0185 (7)	−0.0516 (3)
C(12)	0.2454 (3)	−0.1809 (7)	−0.0334 (4)
C(13)	0.2623 (3)	−0.2395 (6)	0.0555 (4)
C(14)	0.2605 (2)	−0.1333 (5)	0.1238 (3)
C(15)	0.2718 (2)	−0.1907 (6)	0.2202 (3)
C(16)	0.3977 (2)	−0.0194 (6)	0.3244 (3)
C(17)	0.4277 (2)	−0.1113 (6)	0.2735 (3)
C(18)	0.4996 (2)	−0.0928 (6)	0.2869 (3)
C(19)	0.5415 (2)	0.0144 (6)	0.3508 (3)
C(20)	0.5121 (2)	0.1064 (6)	0.4017 (3)
C(21)	0.4405 (2)	0.0920 (5)	0.3900 (3)
C(22)	0.4103 (2)	0.1960 (6)	0.4467 (3)
C(23)	0.4298 (3)	0.4182 (7)	0.5500 (4)

in Table I, and further details are found in supplementary material Table S1. The data were corrected for Lorentz and polarization effects but not for absorption of extinction. Intensity variation of three check reflections was negligible. The structure was solved by direct methods by using the SHELXS 86[18] program and subsequent difference Fourier synthesis. Least-squares refinements were performed using the XTAL program system,[19] which minimized the function $\sum w(|F_o| - |F_c|)^2$, where $w = (1/\sigma_F)$. The neutral-atom scattering factors were those included in the programs. Refinements of all non-hydrogen atoms with anisotropic temperature factors gave an R value of 0.055 ($R_w = 0.054$). The hydrogen atoms were found from the subsequent difference Fourier map. After refinement of these atoms, with anisotropic temperature factors for the non-hydrogen atoms and isotropic temperature factors for the hydrogen atoms, the final R value was 0.041 ($R_w = 0.032$). The greatest maximum in the final difference Fourier map was 0.34 e Å^{-3}.

Results

The reaction of 2,6-bis(bromomethyl)pyridine with thiophenol and thiophenol derivatives (2-(methoxycarbonyl)thiophenol and *p*-chlorothiophenol) yields podand ligands containing the coordinating group NS_2: 2,6-Bis((phenylthio)methyl)pyridine (L1), 2,6-bis(((4-chlorophenyl)thio)methyl)pyridine (L2), and 2,6-bis(((2-(methoxycarbonyl)phenyl)thio)methyl)pyridine (L3). Scheme I exemplifies these reactions.

Repeated column chromatography in different media did not yield the pure compounds except for L3. To overcome this difficulty, the Cu(II) complexes were obtained for L1 and L2, which were later destroyed with CN^- to afford the pure ligands. Scheme II exemplifies these reactions.

The reaction of L1–L3 with $CuCl_2 \cdot 2H_2O$ in a 1:1 molar ratio in methanol yielded complexes of the stoichiometry $LCuCl_2$ with colors ranging from brown to red depending on the substituent on the aryl group. The slow addition of 0.05 M KCN solution to a suspension of $LCuCl_2$ (L = L1, L2) in methanol yield yellow compounds of formula LCuCN, while the demetalated ligand molecules are obtained with an excess of KCN, as it is explained in the Experimental Section. Violet compounds with the stoichiometry $LCu(ClO_4)_2 \cdot 2H_2O$ (L = L1, L2) or $L3Cu(ClO_4)_2$ were obtained upon the reaction of L1–L3 with $Cu(ClO_4)_2 \cdot 6H_2O$ in ethyl acetate. No metal complexes were obtained when ligands L1, L2, and L3 were made to react with Ni(II) or Co(II) salts.

Discussion

As indicated in the Introduction, relatively little is known about the reactivity and stereochemical preferences of tricoordinating ligands of the type NS_2. Our former results with 2,6-bis((ethylthio)methyl)pyridine (2etmp)[2] and the macrocycles MO1 and MO2[10] (Figure 1) indicated that those ligands forced pentacoordination on the copper. The complexes adopted either trigonal-bipyramid or square-planar pyramidal geometries. All these NS_2 ligands had the sulfur elements connected to alkyl fragments, and the way that the replacement of one alkyl by one aryl would affect the stereochemical preferences and physical properties of the resulting complexes was not known. Expectedly this change would soften the sulfur atoms with regard to the similar NS_2 ligands (all alkyl substituents), and a different behavior would be expected either in their ability to coordinate and/or in the physical and geometric characteristics of the resulting complexes.

In the following discussion we will compare these ligands with the similar NS_2 ones (all alkyl substituents) and we will differentiate them simply by indicating L(*S*-alkyl) or L(*S*-aryl).

We have not observed substantial differences in their reacting ability toward copper(II) ions, except in the color of the resulting solids, which tend to be red in the L(*S*-aryl) and green-blue in the L(*S*-alkyl) complexes. However, that color change suggests a change either in the stereochemistry of the copper ion and/or in the electronic characteristics of the resulting copper complex. To unambiguously know the geometrical arrangement of those complexes, the crystal and molecular structure of [(L3)$CuCl_2$] was solved. Figure 2 shows a perspective view of the title molecule.

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(19) Hall, S. R.; Stewart, J. M., Eds. XTAL26 User's Manual. Universities of Western Australia and Maryland, 1987.

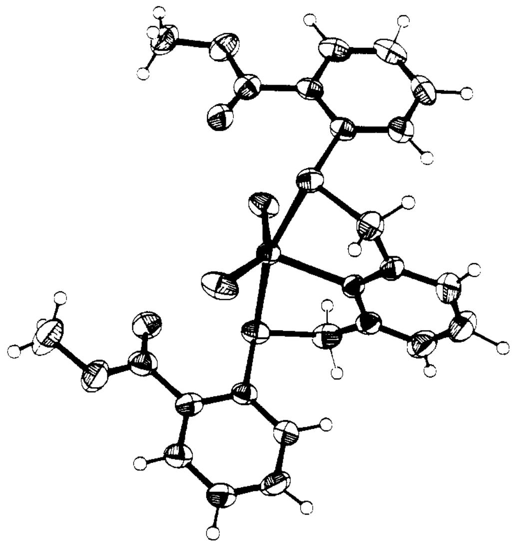

Figure 2. Perspective view for the title molecule [(L3)$CuCl_2$] in the form of an ORTEP drawing. Thermal ellipsoids are drawn with surfaces at the 50% probability level.

Table III. Selected Bond Lengths (Å) and Angles (deg) with Their Estimated Standard Deviations (Esd's) for [(L3)$CuCl_2$]

Cu(1)–S(1)	2.409 (1)	C(2)–C(3)	1.488 (6)
Cu(1)–S(2)	2.431 (1)	C(3)–C(4)	1.407 (6)
Cu(1)–Cl(1)	2.246 (2)	C(3)–C(8)	1.396 (7)
Cu(1)–Cl(2)	2.238 (1)	C(4)–C(5)	1.377 (6)
Cu(1)–N(1)	2.164 (4)	C(5)–C(6)	1.369 (8)
S(1)–Cu(1)–S(2)	163.57 (5)	S(1)–Cu(1)–Cl(1)	100.18 (5)
S(1)–Cu(1)–Cl(2)	85.67 (5)	S(1)–Cu(1)–N(1)	81.78 (9)
S(2)–Cu(1)–Cl(1)	84.95 (5)	S(2)–Cu(1)–Cl(2)	98.82 (5)
S(2)–Cu(1)–N(1)	81.80 (9)	Cl(1)–Cu(1)–Cl(2)	146.09 (6)
Cl(1)–Cu(1)–N(1)	106.0 (1)	Cl(2)–Cu(1)–N(1)	107.9 (1)
Cu(1)–S(1)–C(8)	108.2 (1)	Cu(1)–S(1)–C(9)	95.4 (1)
Cu(1)–S(2)–C(15)	94.5 (1)	Cu(1)–S(2)–C(16)	108.2 (2)
Cu(1)–N(1)–C(10)	120.4 (3)	Cu(1)–N(1)–C(14)	120.0 (3)

Table IV. Coordination Polyhedron Characteristics of the Complexes [(L3)$CuCl_2$] and [(2etmp)$CuCl_2$]

	[(L3)$CuCl_2$]	[(2etmp)$CuCl_2$]
Cu–S(1), Å	2.409 (1)	2.344 (4)
Cu–S(2), Å	2.431 (1)	2.358 (4)
Cu–Cl(1), Å	2.246 (2)	2.242 (4)
Cu–Cl(2), Å	2.238 (1)	2.428 (3)
Cu dist to plane S–N–S, Å	0.02	0.36
Cu dist to plane of Cl–N–Cl, Å	0.04	0.01
Cl dist to plane S–N–S, Å	−2.21	2.77
Cl dist to plane S–N–S, Å	2.09	0.02
dihedral angle S–N–S/Cl–N–Cl, deg	81.52	90.85
color	red	green

Final atomic parameters are reported in Table II. Selected distances and angles are reported in Table III.

The molecular structure consists of discrete molecules containing a copper atom in a distorted trigonal-bipyramid geometry. Each cooper atom is coordinated to two chlorine and sulfur atoms and one nitrogen atom. The phenyl groups bonded to the sulfur elements are placed in an anti fashion in a manner similar to that found in the analogous L(*S*-alkyl) [2,6-Bis((ethylthio)methyl)-pyridine]dichlorocopper(II) complex.[2]

As can be seen in Table IV, where the surrounding characteristics of both copper complexes are presented, there are significant geometrical differences between one complex and the other. The most apparent are the copper distance to the plane S–N–S, the Cl distances to the plane S–N–S, and the dihedral angle defined by planes S–N–S and Cl–N–Cl. The in-plane S–N–S disposition of the copper atom in [(L3)$CuCl_2$] permits one to classify this molecule as trigonal bipyramidal. On the contrary, the coplanarity of the Cl atom with the S–N–S plane in [2,6-bis((ethylthio)methyl)pyridine]dichlorocopper(II)[2] points to a square-planar geometry. Both stereochemistries are slightly distorted; however, they represent a remarkable example of different geometries achieved with identical environments. Figure 3 schematically represents both surroundings. As the level 0, we have taken that with the largest number of coplanar atoms.

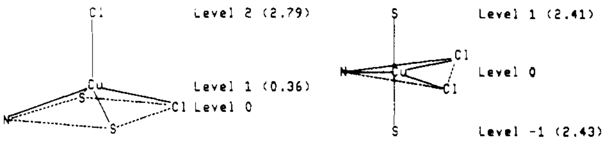

Figure 3. Coordination polyhedron characteristics of the complexes [(L3)$CuCl_2$] and [(2etmp)$CuCl_2$].

Table V. UV–Vis Spectral Absorptions (in nm) for the Complexes in CH_3NO_2 Solution with ϵ Values in Parenthesis[a]

complex	LMTC	d–d
[(L1)Cu(ClO_4)$_2$]·H_2O	485 (2400)	634 (1300)
[(L2)Cu(ClO_4)$_2$]·H_2O	494 (1940)	635 (1240)
[(L3)Cu(ClO_4)$_2$]	453 (1360)	623 (290)
[(L1)$CuCl_2$]	446 (1360)	831 (401)
[(L2)$CuCl_2$]	441 (740)	836 (210)
[(L3)$CuCl_2$]	462 (1200) (s)	758 (270)
[(MO1)$CuCl_2$]	381 (1250)	766 (290)
[(MO2)$CuCl_2$]	400 (1440)	705 (349)
[(2etmp)$CuCl_2$]	398 (2480)	772 (418)

[a] s = shoulder.

Table VI. Formal Reduction Potentials (vs SSCE) for the Couple Cu(II)/Cu(I)

complex	E_f(Cu(II)/Cu(I)), V	complex	E_f(Cu(II)/Cu(I)), V
[(L2)Cu(ClO_4)$_2$]·H_2O	0.72	[(L1)$CuCl_2$]	0.45
[(L3)Cu(ClO_4)$_2$]	0.70	[(MO2)$CuCl_2$]	0.22
[(L1)Cu(ClO_4)$_2$]·H_2O	0.69	[(2etmp)$CuCl_2$]	0.15
[(L2)$CuCl_2$]	0.52	[(MO1)$CuCl_2$]	0.14
[(L3)$CuCl_2$]	0.52		

Table VII. EPR *g* and *a* Values[a]

complex	*g*	*a*, 10^{-4} cm^{-1}
[(2etmp)$CuCl_2$]	2.17	93.20
[(MO1)$CuCl_2$]	2.09	77.08
[(L1)Cu(ClO_4)$_2$]·H_2O	2.09	74.81
[(L3)Cu(ClO_4)$_2$]	2.10	72.73
[(L2)Cu(ClO_4)$_2$]·H_2O	2.10	71.73
[(L3)$CuCl_2$]	2.08	65.58

[a] The complexes [(MO2)$CuCl_2$], [(L1)$CuCl_2$], and [(L2)$CuCl_2$] are not sufficiently soluble in nitromethane to run EPR spectra.

As can be seen in Table V, the visible spectra of the chloride complexes present a marked difference in the position of the σ(S) → $d_{x^2-y^2}$ band (400–381 nm, L(*S*-alkyl); 462–446 nm, L(*S*-aryl)), while the d–d band does not give any clue about the nature of the ligand. Consequently, the observed changes in the colors of the complexes are mainly due to the LMCT σ(S) → $d_{x^2-y^2}$. These data suggest a considerable electronic difference between the L(*S*-alkyl) and L(*S*-aryl) complexes reported here. This dissimilarity becomes even more obvious when the cyclic voltammetry and EPR spectra are studied. Tables VI and VII present CV and EPR data for both types of compounds. Values ranging from 0.72 to 0.14 V are encountered in those compounds. Significantly, all L(*S*-aryl) compounds present higher voltages for the couple Cu(II)/Cu(I) than those found for L(*S*-alkyl), which certainly implies an enhanced capacity for stabilizing low oxidation states so they are softer. A similar conclusion can be drawn from the EPR data concerning the "*a*" values. According to the literature,[20] the *a* value is dependent upon the π acidity of the ligand; the higher this is, the smaller is the *a* value. As a result, we should expect

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(20) Swett, V. C.; Dudeck, E. P. *J. Phys. Chem.* **1968**, *72*, 1244.

smaller *a* values for our L(*S*-aryl) compounds than for L(*S*-alkyl), which effectively happens (93×10^{-4} cm^{-1} for [(2etmp)$CuCl_2$]; 65.5×10^{-4} cm^{-1} for [(L3)$CuCl_2$]). The relatively high *a* values for the perchlorate complexes are attributed to oxygen coordination to Cu(II). A nonsplitting of the EPR signals by the pyridinic nitrogen atom is observed. This certainly implies a strong overlap of the metal $d_{x^2-y^2}$ orbital with the appropriate sulfur atomic orbital. Again these data are in agreement with the CV and visible spectra reported.

As a conclusion, the substitution of *S*-alkyl groups in 2,6-bis(thiomethyl)pyridine ligand derivatives by *S*-aryl groups markedly affects the physical and geometrical properties of the resulting copper complexes. Those L(*S*-aryl) ligands are softer and more π acidic than the L(*S*-alkyl) ones. Also, the incorporation of electron-withdrawing elements in the aromatic ring (Cl, COOR) of the *S*-aryl group does not significantly affect the behavior of the pure L(*S*-aryl) ligand. In a future work we will implement these materials as sensors in all-solid-state electrodes to find if these encountered structural and physical differences between L(*S*-alkyl) and L(*S*-aryl) find their counterparts in metal ion selectivity.

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Registry No. L1, 137058-21-0; L2, 137058-22-1; L3, 137058-23-2; [(L1)$CuCl_2$], 137058-24-3; [(L2)$CuCl_2$], 137058-25-4; [(L3)$CuCl_2$], 137091-67-9; [(L1)$Cu(ClO_4)_2$], 137058-26-5; [(L2)$Cu(ClO_4)_2$], 137058-27-6; [(L3)$Cu(ClO_4)_2$], 137058-28-7; [(L1)CuCN], 137058-29-8; [(L2)CuCN], 137058-30-1; [(2etmp)$CuCl_2$], 124406-33-3; [(MO1)$CuCl_2$), 132673-29-1; [(MO2)$CuCl_2$], 132673-34-8; Na, 7440-23-5; thiophenol, 108-98-5; 2,6-bis(bromomethyl)pyridine, 7703-74-4; thiosalicyl methyl ester, 119-36-8; 4-chlorothiophenol, 106-54-7.

Supplementary Material Available: Tables S1–S5, listing crystal data, anisotropic thermal parameters, hydrogen atomic coordinates and thermal parameters, full bond length and bond angle data, and least-squares planes (16 pages); a listing of observed and calculated structure factors (16 pages). Ordering information is given on any current masthead page.

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$[H_3KV_{12}As_3O_{39}(AsO_4)]^{6-}$ and Related Topological and/or Structural Aspects of Polyoxometalate Chemistry

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On reduction of an aqueous solution of vanadate(V) with thiocyanide in the presence of As^V, the black-gray mixed-valence compound $K_6[H_3KV_{12}As_3O_{39}(AsO_4)]\cdot 8H_2O$ (**1**) is formed. It crystallizes in the space group *C*2/*c* with $a = 39.993$ (15) Å, $b = 13.467$ (4) Å, $c = 18.209$ (6) Å, $\beta = 111.52$ (3)°, and $Z = 8$. Refinement of 686 variables with 8827 observed reflections yields $R = 0.049$ and $R_w = 0.058$. The compound contains an anion with approximate C_3 symmetry, which can be described as a fragment of a sphere capped with a potassium ion. The oxygen and/or metal atoms of polyoxometalates often span the vertices of topologically and/or geometrically interesting polyhedra. Related aspects of **1** are discussed.

Introduction

Close-packing effects of atoms as well as related geometrical and/or topological aspects play an important role in structural chemistry.[1] This is very typical for polyoxometalates of the d-group elements which represent one of the most versatile class of compounds if both structural *and* electronic properties are considered.[2] It is especially fascinating, as in most of the species only two or three different atoms are involved. These species also play a role in catalytic processes and many other applications.[2] A special type of chemistry seems to be related to reduced and/or mixed-valence V_xO_y clusters,[2] and in this paper we report the synthesis of a new high-nuclearity species of that type.

Experimental Section

Synthesis of $K_6[H_3KV_{12}As_3O_{39}(AsO_4)]\cdot 8H_2O$ (1). KVO_3 (1.66 g, 12 mmol) was dissolved with stirring in 50 mL of water at 90 °C (100-mL Erlenmeyer flask). After addition of $3As_2O_5\cdot 5H_2O$ (0.52 g, 4 mmol), the clear orange-red solution (pH 5) was stirred for 10 min at 90 °C and KSCN (8.70 g, 89.5 mmol) was added. A pH value of ca. 2 was adjusted by addition of 5 mL of 0.5 M H_2SO_4 (dark green solution). After 45 min at 90 °C (vessel covered with a watch glass), the color changed to deep black and the pH value increased to ca. 3. After cooling, the flask was stored at room temperature. The black-gray bladelike crystals thereby formed were filtered off after 1 day, washed with cold water, and dried in air. Yield: 0.7 g. Anal. Calcd (found): As, 14.0 (14.9); K, 13.1 (13.5); V, 29.8 (30.3). IR (KBr pellet; cm^{-1}): 3700–3200 (vs, br), ν(OH); 1605 (m), δ(HOH); 963 (s), ν(V=O); 898 (m), ν(As—O-(AsO_4^{3-})); 856 (s), 835 (s), 720 (m), 662 (m), ν_{as}(M—O—M (M = V, As)) and ν(As—O(H)).

Table I. Crystallographic Data for $K_6[H_3KV_{12}As_3O_{39}(AsO_4)]\cdot 8H_2O$ (**1**)

formula	$As_4H_{19}K_7O_{51}V_{12}$	space group	*C*2/*c* (No. 15)
fw	2019.8	*T*, K	294
a, Å	39.993 (15)	λ, Å	0.71073
b, Å	13.467 (4)	ρ_{calc}, g·cm^{-3}	2.94
c, Å	18.209 (6)	μ, cm^{-1}	59.1
β, deg	111.52 (3)	R^a/R_w^b	0.049/0.058
V, Å^3	9124	no. of obsd reflns	8827 ($F_o > 4\sigma(F_o)$)
Z	8		

[a] $\sum||F_o| - |F_c||/\sum|F_o|$. [b] $(\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2)^{1/2}$; $1/w = \sigma^2(F_o) + 0.0001F_o^2$.

Manganometric Titration. The V^{IV} content of **1** was determined by titration of a solution of 50 mg of **1** in dilute H_2SO_4 (10%) at 65 °C with 0.1 N $KMnO_4$. The redox reaction was potentiometrically followed with a Mettler instrument (Memo Titrator DL 40) using a Pt electrode against an SCE.

X-ray Structure Determination of 1. Data for **1** were measured at room temperature on a Siemens R3m/V four-circle diffractometer with a graphite monochromator and Mo Kα radiation ($\lambda = 0.71073$ Å). Empirical absorption corrections (ψ-scans) were applied, and the SHELXTL PLUS program package[3] was used for structure solution (direct methods) and refinement. The hydrogen positions of the anion in **1** were determined as stated in Table II. In the crystal lattice of **1**, some of the potassium ions and water molecules are disordered. K(7), K(7A), K(8),

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(1) Wells, A. F. *Structural Inorganic Chemistry*; Clarendon Press: Oxford, U.K., 1984. Wells, A. F. *Three-Dimensional Nets and Polyhedra*; John Wiley & Sons: New York, 1977. The borderline between geometry and topology is indistinct (Flegg, H. G. *From Geometry to Topology*; The English Universities Press: London, 1974; cf. ref 6).

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