Table III. Bond Length Changes (Δr) in Tetrahedral Ions on Excitation

ion	resonant transition	Δr/Å	ref
$[MnO_4]^-$	$^1T_2 \leftarrow {}^1A_1$	0.046	1
$[MnO_4]^{2-}$	$^2T_2 \leftarrow {}^2E$	0.035	this work
$[MoS_4]^{2-}$	$^1T_2 \leftarrow {}^1A_1$	0.035	2
$[WS_4]^{2-}$	$^1T_2 \leftarrow {}^1A_1$	0.029	5

calculated that $\Delta r = 0.044 \pm 0.002$ Å. Martin and Onari[12] fitted their resonance Raman data by a Franck–Condon analysis using a value of $\Delta^2 = 3.0$. This corresponds to a bond length change $\Delta r = 0.063$ Å, which is clearly too large. The higher Δr values obtained from the analysis of the absorption spectra are most probably due to the overlap of the main $\nu_1\nu_1$ progression by $\upsilon_1\nu_1 + \nu_3$. The latter is not resolved because of the close proximity of ν_1 to ν_3 but must nevertheless be present (vide supra). Its presence would increase the intensities of the 0_g–υ_e peaks relative to that of the 0_g–0_e one, thus producing an erroneously high value for Δr.

The bond length changes in tetrahedral ions attendant upon excitation to the lowest (electric dipole allowed) charge-transfer state are given in Table III. The values listed are a factor of 2 smaller than those given in the original electronic[22] and resonance Raman papers[1,2,5] owing to the use in these papers of an incorrect relation between Δr and ΔQ_1. The bond length change calculated for $[MnO_4]^{2-}$ is ~25% lower than that for $[MnO_4]^-$. It is not clear why this should be since, in both cases, the excitation involves the same pair of orbitals. Moreover, Δr for $[MnO_4]^-$ is about 50% greater than that established crystallographically (0.03 Å) to accompany one-electron reduction of $[MnO_4]^-$ to $[MnO_4]^{2-}$, each in their ground state.[23] In common with $[MnO_4]^-$ the excitation profiles are best reproduced by assuming that the broadening mechanism is exclusively homogeneous. Introduction of inhomogeneous broadening resulted in much higher value for $I(2\nu_1)/I(\nu_1)$ in the preresonance region than is observed experimentally. Introduction of inhomogeneous broadening resulted in much higher value for $I(2\nu_1)/I(\nu_1)$ in the preresonance region than is bserved experimentally.

No resonance enhancement was observed for excitation within the contour of the next strong absorption band of the $[MnO_4]^{2-}$ ion, at around 24 000 cm^{-1}. This absorption results from the superposition of the second lowest energy $^2T_2 \leftarrow {}^2E$ band and the lowest energy $^2T_1 \leftarrow {}^2E$ band. The lack of resonance enhancement in this region may be due to destructive interference between the contributions to the transition polarizability from the $^2T_2$ and $^2T_1$ and other nearby states.

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Registry No. $[MnO_4]^{2-}$, 14333-14-3; $K_2[CrO_4]$, 7789-00-6.

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Contribution from the Laboratoire de Chimie de Coordination
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Metal Complexes of Rubeanic Acid. 3.[1] Large-Angle X-ray Scattering Studies of Amorphous Copper(II) and Nickel(II) Complexes

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Two amorphous complexes of the dithiooxamide ligand (rubeanic acid) have been prepared and studied: $Cu(C_2S_2N_2H_2)(H_2O)$ and $Ni_4(C_2S_2N_2H_3)_2(C_2S_2N_2H_2)_3(H_2O)_{0.25}$. Both compounds have essentially the same local structure. The proposed structural model can be described by the following features: (i) the ligand is in a trans conformation and planar; (ii) the coordination is ensured by the four donor atoms (S, N), and the Ni environment is square planar; (iii) the ribbons thus formed stack perpendicularly to the ligand plane with an interval equal to 3.6 Å.

Introduction

The complexes of rubeanic acid (dithiooxamide) have been used in analytical chemistry for a long time,[2,3] but their magnetic,[4] semiconducting,[5] and catalytic[6] properties have only recently been accounted for and have induced new searches on their structure. Very little is known about their geometry due to the extreme difficulty in growing single crystals; the metallic complexes of the nonsubstituted rubeanic acid are insoluble in most common solvents. Consequently, they are always obtained in the amorphous state or as a very poorly crystalline powder. Numerous solution- and solid-state studies have been performed by using various spectroscopic methods to settle the systematics of the coordination modes of the rubeanic acid ligand.[7-9] These studies proposed various structural hypotheses, but it has not been made possible to check them through an experimental single-crystal X-ray diffraction investigation.

Table I. Chemical Analysis of the Copper and Nickel Complexes

M		C	H	N	S	M
Cu	% found	12.85	1.55	14.13	33.78	32.5
	% calcd[a]	12.02	2.01	14.02	32.10	31.8
Ni	% found	13.99	1.65	15.83	35.16	27.88
	% calcd[a]	14.16	1.66	16.51	37.80	27.68

[a] Calculated with respect to the formulas $Cu(C_2N_2S_2H_2)(H_2O)$ and $Ni_4(C_2N_2S_2H_3)_2(C_2H_2S_2H_2)_3$.

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Subsequent to a thorough study of the crystallogenesis of these products,[10] it has finally been possible to isolate two crystalline complexes of copper(I), $CuCl(C_2N_2S_2H_4)_{1.5}(H_2O)_{0.45}$ and $CuCl(C_2N_2S_2H_4)$, and to determine their detailed crystal structure.[1]

Knowing the coordination mode of the ligand and the precise bond length and bond angles, it was then possible to tackle the problem of the structure of copper(II) and nickel(II) complexes in their amorphous form by the LAXS technique (large-angle X-ray scattering).

Experimental Section

The two amorphous compounds presented here have been synthesized by mixing system's solutions of the ligand and of metal acetate (molar ratio 1:1). The precipitation was instantaneous at room temperature. The precipitate was successively washed with a dilute alkaline solution and with distilled water and dried at 60 °C.

Chemical analyses of the two compounds (Table I) are in agreement with the formulas $Cu(C_2N_2S_2H_2)(H_2O)$ and $Ni_4(C_2S_2N_2H_3)_2(C_2S_2N_2H_2)_3(H_2O)_{0.25}$.

The carefully crushed amorphous powders were pressed into pellets under 3 kbar of pressure and were directly utilizable for the registration of X-ray diffuse spectra (thickness of the pellets: $e_{Cu} = 0.30$ mm, $e_{Ni} = 0.27$ mm).

The diffuse spectrum scattered by the sample irradiated with graphite-monochromatized molybdenum Kα radiation was obtained by using an automatic diffractometer. About 450 intensities corresponding to equidistant s points ($s = 4\pi(\sin\theta)/\lambda$; $\Delta s = 0.035\,363$) were collected (in the range $0.617 < s < 16.615$ Å^{-1}. The stability of the X-ray flux and of the sample was checked by frequent repetition of measurements at angles conveniently spread out in the θ range. All the measurements were carried out at 22 °C.

Scattered intensities were corrected for polarization and absorption effects (namely $I_c(s)$) and then normalized by comparison with the sum of coherent and incoherent independent intensities in the vicinity of high θ angles.

The reduced intensities, $i(s)$, were calculated as follows:

$$i(s) = KI_c(s) - \sum_i n_i[(f_i(s) + \Delta f'_i)^2 + \Delta f''^2_i + I_{i(\mathrm{incb})}(s)]$$

where K is the normalization constant, $I_c(s)$ is the corrected intensities, n_i is the number of atoms i in the chosen unit volume, $f_i(s)$ is the atomic scattering factor, $\Delta f'_i$ and $\Delta f''_i$ are the real and imaginary parts of the anomalous dispersion, and $I_{i(\mathrm{incb})}(s)$ is the total incoherent radiation for atom i. The radial distribution, $D(r)$, is then expressed in the form

$$D(r) = 4\pi r^2\rho_0 + 2r\pi^{-1}\int_{s_{\min}}^{s_{\max}} s\, i(s)\, M(s) \sin(rs)\, \mathrm{d}s$$

where ρ_0 is the average electronic density of the sample and $M(s)$ is a modification function defined by $[f^2_{Ni}(0)/f^2_{Ni}(s)][\exp(-s^2/100)]$.

The corresponding theoretical intensities were calculated from the relation

$$i(s) = \sum_i\sum_j f_i(s)\, f_j(s) \frac{\sin(r_{ij}s)}{r_{ij}s} \exp(-b_{ij}s^2)$$

where r_{ij} is the interatomic distance between atoms i and j and b_{ij} is a temperature factor affecting this interaction.

Other details on the data processing are given elsewhere.[11,12] All the calculations have been performed on an Apple II microcomputer using our LASIP (liquid and amorphous structure investigation package) system.[13]

Results and Discussion

Development of a Structural Model. The lack of structural elements concerning the nonsubstituted rubeanic acid complexes with copper(II) or nickel(II) does not allow us to establish an a priori model for these amorphous phases. It is then necessary to investigate the most plausible coordination schemes for the ligand in the light of the literature information.

Six main structural models are proposed after such a survey (Figure 1).

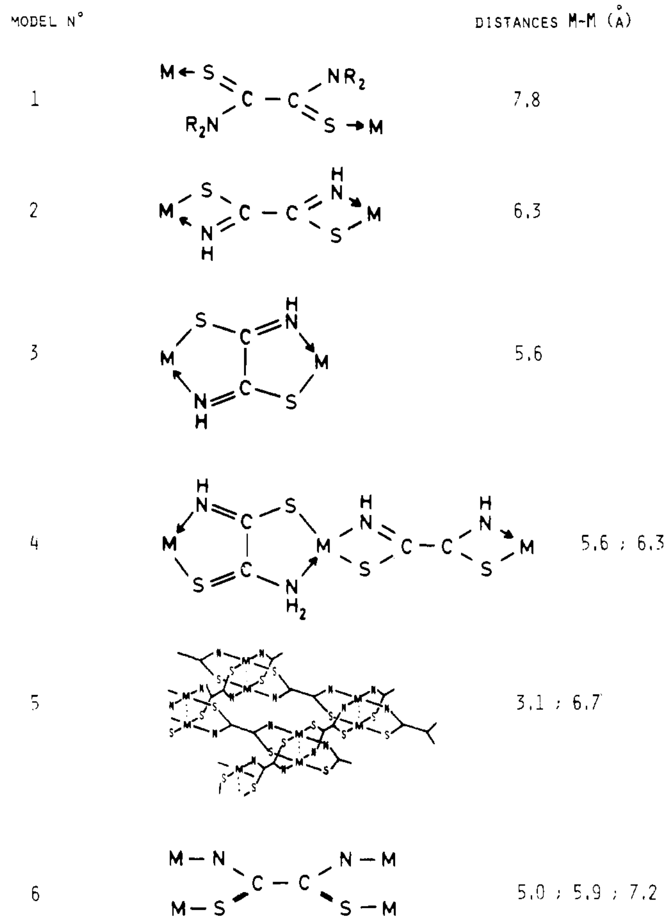

Figure 1. Coordination models proposed for rubeanic acid.

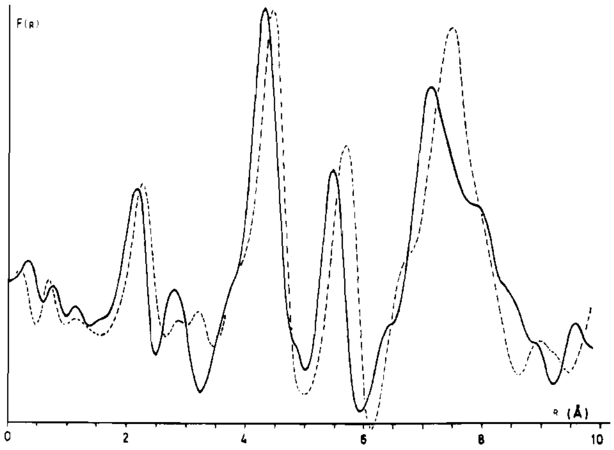

Figure 2. Experimental radial distribution functions (RDF) for the Ni complex (full line) and for the Cu complex (dotted line).

Model 1 corresponds to a trans bidentate ligand coordinated by the sulfur atoms only, which leads to a polymer characterized by a metal–metal distance close to 7.8 Å. Such a coordination mode has been suggested only for cadmium and mercury complexes;[14] it has been observed and has been well-defined for copper(I) complexes.[1]

Models 2 and 3 exhibit a tetracoordination of the ligand in a trans conformation again occurring on two metallic centers. The resultant "polymers" show metal–metal distances equal to 6.3 and 5.6 Å, respectively. It is reasonable to state that model 2 appears thermodynamically less favorable due to the occurrence of four-bond rings.

Model 4 is a combination of the coordination schemes illustrated in models 2 and 3 but implies a cis conformation for the ligand. This model has been suggested for platinum and palladium com-

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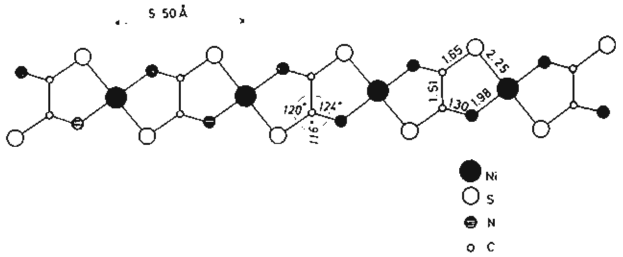

Figure 3. Geometry of the chain chosen as initial model.

plexes[15] but has never been observed by X-ray scattering studies.

Finally, models 5 and 6 impose a tetracoordination of the ligand on four metallic centers. Model 5 gives metallic interations at about 3.1 Å, analogous to those already observed in the copper acetate. Model 6 implies a cis conformation.

None of these models can be ignored for crystallographic or chemical reasons. The many plausible solutions require a detailed analysis of the experimental results, i.e. the radial distribution functions issued from LAXS analysis, prior to the choice of a structural model for our compounds.

The experimental radial distribution functions (RDF) of both the copper(II) and the nickel(II) compounds are shown in Figure 2.

Clearly, the internal architectures of both compounds appear very similar. The shifts of the peak positions can be explained by some variations in the coordination bonds. Differences in the intensity of the main peaks are attributed to variations of chain lengths, as will be underlined hereafter.

The first peak of the RDF is centered around the mean value 2.2 Å; it is the result of an accumulation of the metal–sulfur and metal–nitrogen coordination distances. The three other main peaks are centered around 4.4, 5.6, and 7.3 Å. Because of their relative importance, it is most likely that they result, at least partially, from a multiple superposition of metal–metal interactions. These distances for the various hypothetical models are listed in Figure 1.

(i) The peak centered at 4.4 Å cannot be explained by one of the models. Possible intermolecular or interchain interactions then have to be taken into account. This is seen in the crystal chemistry of metallic complexes involving a parent ligand of rubeanic acid, such as oxalic and dithiooxalic acids; i.e., in the alkali-metal dithiooxalates $K_2Ni(S_2C_2O_2)_2$, the Ni–Ni distance is equal to 4.2 Å.[15]

(ii) Models 2, 4, 5, and 6 can be rejected as unlikely: the values of metal–metal distances (6.3, 3.1, 5.0, and 5.9 Å, respectively) correspond to "valleys" in the RDF. Model 1 partially explains the bulk centered at 7.3 Å but provides no element to simulate the beginning of the curve.

(iii) The peak at 5.6 Å is explained by model 3, which moreover generates no "forbidden" distances.

(iv) The cis conformation of the ligand is unlikely for several reasons. All the single-crystal structure studies on the free ligand[16] and on the complexes[1] show a trans conformation. The IR spectrum study and the normal-coordinate analysis of the nickel complex[17,18] lead to the same conclusion. Moreover, the cis conformation would generate a strong accumulation of S–S interactions at 3.1–3.2 Å and cancel S–S contributions at 4.3 Å, in disagreement with the experimental RDF.

These preliminary remarks allow us to elaborate a prototype for the amorphous structure of the compounds defined by the following criteria and schematized by Figure 3: bond lengths and bond angles are those determined by the studies of copper(I) complexes;[1] the rubeanic acid ligand is in a trans conformation; the coordination scheme follows model 3 and gives rise to the formation of polymeric ribbons; the ribbons are stacked in such a way that accumulations of interatomic distances around 4.4 and 7.3 Å are obtained.

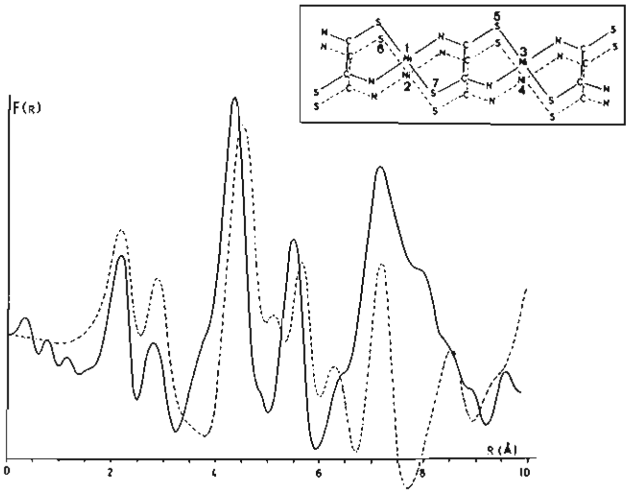

Figure 4. Nickel complex, initial model: experimental RDF, full line; theoretical RDF, dotted line.

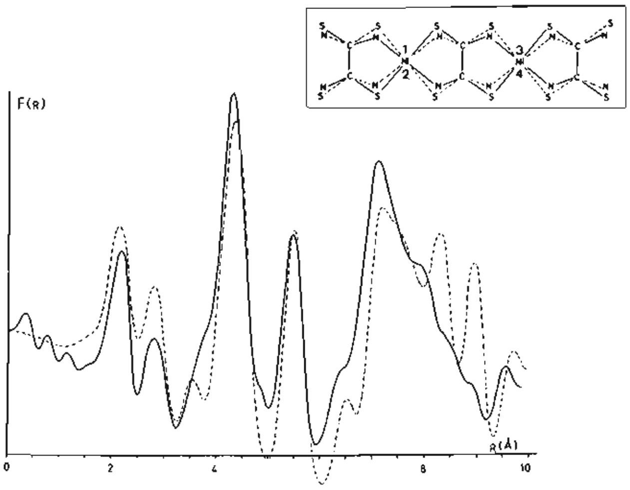

Figure 5. Nickel complex, final model: experimental RDF, full line; theoretical RDF, dotted line.

Study of the Nickel(II) Complex. In a first attempt, only two chains have been taken into account, which are identical with those described in Figure 3. Their relative positions are defined by including constraints for metal–metal and metal–sulfur distances (see inset in Figure 4): Ni(3)–Ni(4) = 4.30 Å; Ni(4)–S(7) = 5.50 Å. The resulting theoretical RDF is represented in Figure 4. Comparison with the experimental RDF induces the following remarks: the peaks at 4.4 and 5.6 Å are slightly shifted, which implies imprecisions in the relative packing of the chains; the agreement between experimental and theoretical RDF curves at the level of the massive peak (7.3 Å) is very poor, and it appears necessary to add a third chain to get a better definition of the model; the peaks of the theoretical curves around 4.4 and 5.6 Å are too weak, and the model does not supply grounds for the peak shoulder at 3.7 Å.

All the models tested in which the second chain is simply deduced by a translation exhibit the same defect.

A good correlation has finally been obtained by elaborating the following model: The second chain is deduced from the original one after a translation of 3.6 Å in the direction perpendicular to the average plane of the chain and a 180° rotation around the chain axis. As illustrated in the inset of Figure 5, such operation leads to the superposition of the nickel atoms one above the other and of the sulfur atoms above the nitrogen atoms. The metal–metal distances are then Ni(3)–Ni(4) = 3.6 Å and Ni(3)–Ni(2) = 6.7 Å. The extended model, i.e. three chains, gives the theoretical RDF illustrated by Figure 5.

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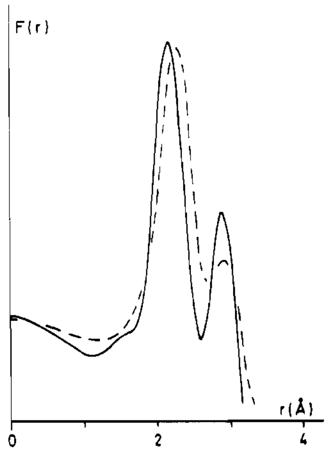

Figure 6. Partial theoretical RDF for the Cu complex (dotted line) and the Ni complex (full line). The geometry of the ligand for the copper complex is taken from ref 20.

The agreement between experimental and theoretical curves becomes rather good up to 6 Å and "acceptable" up to 8 Å. Above 8 Å, the curves show discrepancies.

The critical analysis of the structural model which is finally adopted to explain the discrepancies is summarized hereafter.

(i) The model is quite symmetrical: all rubeanic acid ligands have the same geometry, the metals have a regular environment, the chains are strictly planar, and the interstack distance is supposed constant. Such a situation is of course too perfect to fit with the structural organization of the amorphous material. Slight variations in the model attenuate the peaks at 2.8, 3.7, and 6.5 Å, broaden the peaks at distances such as 8 and 9.5 Å, or give shoulders.

(ii) The interactions between chains in directions other than the stacking are not taken into account, because of the tremendous amount of parameters involved. Anyhow, these interactions exist and may contribute to explain the discrepancies observed above 8 Å.

Study of the Copper(II) Complex. As illustrated by Figure 2, the copper(II) and the nickel(II) complexes have similar amorphous structural architectures. A new model has not been defined, and reasonable explanations of the slight divergences are only tentatively proposed.

(i) The shift of the peaks, between the two RDF's, does not exceed 0.2 Å and can be associated with the different coordination bonds and the correlative variation of the interatomic distances. Average bond lengths of 2.16 Å for the nickel complex and 2.25 Å for the copper complex have been observed.

(ii) A noticeable change appears in the region of 3 Å when the peak at 2.8 Å for the nickel is substituted by two oscillations, one above and one below 3 Å. This peak is essentially due to metal–carbon interactions. The number of such contributions, for one metal center, diminishes from 4 in the nickel complex to 3.5 in the copper complex. Moreover, as already mentioned, small variations of the geometry induce attenuation of the peaks; it seems that the rubeanic acid ligand is less symmetrical in the copper complex. The effect of these factors is illustrated in Figure 6.

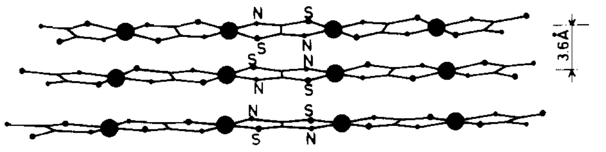

Figure 7. Scheme of the final model proposed.

(iii) The peaks at 5.65 and 7.40 Å are more intense for the copper complex (the coordination peak is taken as a standard). For the first peak, this can be related to the length of the chains with a number of metal–metal interactions, per metal center, equal to 1 in the copper complex and 0.75 in the nickel one. Such an argument may also be proposed for the peak centered around 7.4 Å.

Conclusion

To conclude this study of the amorphous complexes of copper(II) and nickel(II) with rubeanic acid, it is important to recall that the LAXS investigation does not allow us to obtain a univocal correlation between the RDF and the three-dimensional organization of the material. Anyhow, the analysis of the crystal chemistry of analogous compounds, the rather important amount of tested theoretical models, and the good agreement between experimental and theoretical curves allow us to assign a high reliability index to the proposed model.

The final model described in Figure 7 is characterized by the following points: the rubeanic acid ligand is quasi-planar and in a trans conformation; the coordination is effective through the two sulfur and the two nitrogen atoms, giving rise to the formation of polymeric chains; at a "short" range order these chains stack with an interval of ca. 3.6 Å; the chain length is more important in the case of the copper complex; relative freedom of the local structure, i.e. variations in bond lengths and bond angles, slight deviations to the planarity, deviations and faults in the stacking, etc., has to correct the too symmetrical features of the model in order to explain the amorphous nature of the material studied.

The nickel complex is a poor conductor ($\sigma = 10^{-9}\ \Omega^{-1}\ \mathrm{cm}^{-1}$) while the copper complex is a semiconductor ($\sigma = 10^{-4}\ \Omega^{-1}\ \mathrm{cm}^{-1}$). The interchain distance is not very important, 3.6 Å, and could explain the σ value observed for the nickel complex. In the case of the copper complex, the semiconducting properties could be associated with the possibility of some electron delocalization through the ligand by overlapping the sulfur and nitrogen orbitals as already underlined in analogous compounds.[19,20]

Registry No. $C_4(C_2S_2N_2H_2)$, 52391-22-7; $Ni_4(C_2S_2N_2H_3)_2(C_2S_2N_2H_2)_3$, 52659-77-5.

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