attributed to a decrease in the density of states at the Fermi level. The data for the samarium solid solution support this view, with $SmMo_6Se_8$ having the highest superconducting transition temperature and the highest χ_0, which can be thought of as the Pauli contribution to the susceptibility and is directly related to the density of states.

In summary, this study clearly shows that samarium is trivalent across the solid solution $SmMo_6S_{8-x}Se_x$. The decreased ordering of the chalcogens observed in this solid solution when compared to that of the lanthanum solid solution is the result of the samarium cation being more delocalized from the symmetry axis. The importance of crystal field effects on the magnetic properties of the samarium in the ternary molybdenum chalcogenides is demonstrated by the reduced moment and the variation of the moment with changes in the symmetry of the samarium cation.

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EPR Spectra of Binuclear Triazolato- and Imidazolato-Bridged Copper(II) Complexes Including the Four-Copper Form of Bovine Erythrocyte Superoxide Dismutase

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Single-crystal EPR spectra of bis[μ-3,5-bis(pyridin-2-yl)-1,2,4-triazolato-N',N^1,N^2,N']bis[aqua(trifluoromethanesulfonato-O)-copper(II)], $[Cu(bpt)(CF_3SO_3)(H_2O)]_2$, were recorded at room temperature. They are typical of a triplet with $g_{xx} = 2.055$ (1), $g_{yy} = 2.051$ (1), $g_{zz} = 2.232$ (1), $D_{x'x'} = 0.0026$ (5) cm^{-1}, $D_{y'y'} = 0.0338$ (3) cm^{-1}, and $D_{z'z'} = -0.0364$ (4) cm^{-1}. The z and z' axes are practically parallel to each other, making an angle of 4 (1)°, while the y and y' axes are rotated by 51 (9)°. The fact that the largest zero-field splitting component is observed parallel to g_{zz}, and orthogonal to the copper–copper direction, is taken as evidence of a dominant exchange contribution, which is propagated by the triazolate bridges between the two copper(II) ions separated by 408.5 pm. The comparison of the EPR spectra of $[Cu(bpt)(CF_3SO_3)(H_2O)]_2$ with those previously reported for $[(TMDT)_2Cu_2(im)(ClO_4)_2](ClO_4)$ and for the four-copper form of bovine erythrocyte superoxide dismutase, Cu_2Cu_2SOD, allows us to suggest an assignment for the latter compounds and shows that even in these cases the exchange contribution to the zero-field splitting is dominant.

Introduction

The mechanism of the exchange interactions between two copper ions bridged by imidazolate, and similar ligands, is currently being intensively investigated.[2-10] In particular, several attempts have been made to correlate the observed values of the isotropic coupling constant J (the spin Hamiltonian will be used in the form $\mathcal{H} = J\mathbf{S}_1\cdot\mathbf{S}_2$) with the electronic structure of the two copper ions, but until now no clear trend has emerged.[11] It has become clear however that relatively strong exchange can be operative even between two copper ions separated by as much as 600 pm. In particular, the singlet–triplet splitting J has been estimated to be 52 cm^{-1} in the four-copper form of bovine erythrocyte superoxide dismutase,[12,13] Cu_2Cu_2SOD, where the metal–metal distance is presumably not too different from 630 pm, the observed[14] copper–zinc distance in the native form of the enzyme, Cu_2Zn_2SOD.

Another field of intense investigation is that of EPR spectroscopy of dinuclear imidazolato-type-bridged copper(II) complexes. It is now well-known that the observed zero-field splitting of the triplet states is determined by both dipolar and exchange effects.[15,16] Contrary to what has been assumed for some time, the exchange contribution to the zero-field splitting tensor **D** is *not* proportional to the isotropic coupling constant, which is determined by the interaction between the two ground magnetic orbitals, but depends on exchange interactions between one ion in its ground state and the other ion in an excited state.[15] This has been proved in complexes with large J and small **D**, and vice versa.[17-19]

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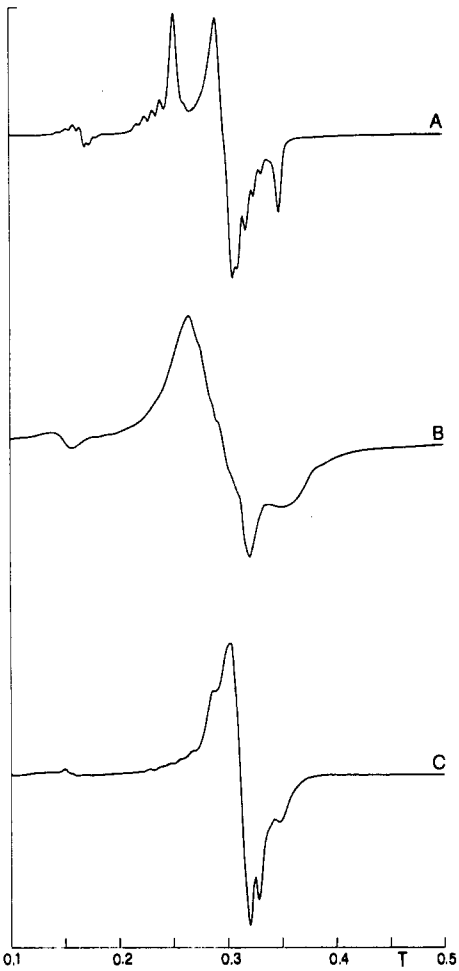

Figure 1. (A) Polycrystalline-powder EPR spectrum of $[Cu(bpt)(CF_3SO_3)(H_2O)]_2$ at X-band frequency and 77 K (from ref 20). (B) Frozen-solution EPR spectrum of Cu_2Cu_2SOD in H_2O at X-band frequency (from ref 24). (C) Polycrystalline-powder EPR spectrum of $[(TMDT)_2Cu_2(im)(ClO_4)_2](ClO_4)$ at X-band frequency and 20 K.

In the case of imidazolato-type-bridged complexes, the study of the EPR spectra is of particular interest, since it can provide useful information as to how the exchange interaction between different magnetic orbitals can be propagated through extended bridges.

Recently we reported[17] the single-crystal EPR spectra of (μ-benzotriazolato-N^1,N^3)bis[[tris((N^1-methylbenzimidazol-2-yl)-methyl)amine-$N,N^3,N^{3'},N^{3''}$]copper(II)] trinitrate, $[Cu_2(tmbma)_2(bta)](NO_3)_3$, and showed that a substantial exchange contribution to the zero-field splitting is present even though the two metal ions are 553.6 pm apart.[7]

We have now studied the EPR spectra of bis[μ-3,5-bis(pyridin-2-yl)-1,2,4-triazolato-N',N^1,N^2,N'']bis[aqua(trifluoromethanesulfonato-O)copper(II)],[20] $[Cu(bpt)(CF_3SO_3)(H_2O)]_2$, which contains two copper ions bridged by two triazolate anions, separated by 408.5 pm, and have observed a singlet–triplet separation of 236 cm^{-1}. Due to the similarity of the EPR spectra of $[Cu(bpt)(CF_3SO_3)(H_2O)]_2$ to those of Cu_2Cu_2SOD[21-24] and (μ-imidazolato)bis[(perchlorato)(1,1,7,7-tetramethyldiethylenetriamine)copper(II)]perchlorate,[3] $[(TMDT)_2Cu_2(im)(ClO_4)_2]$-$(ClO_4)$ (which, although available in the literature for quite some time now, have not been interpreted), we are able to suggest for the first time a tentative assignment of the EPR spectra of Cu_2Cu_2SOD.

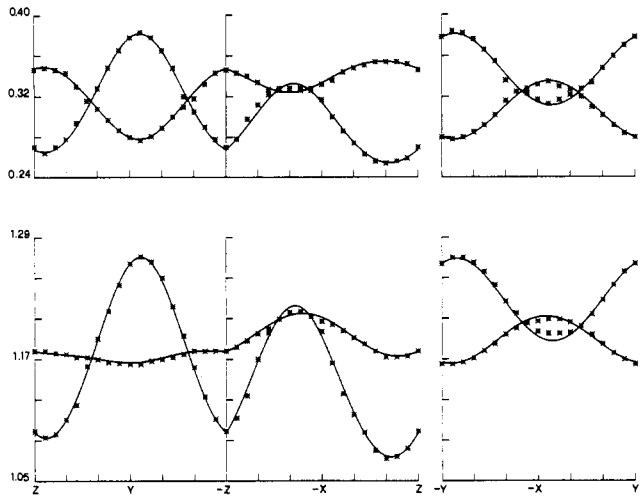

Figure 2. Angular dependence of the transition fields (in T) for $[Cu(bpt)(CF_3SO_3)(H_2O)]_2$: lower, Q-band frequency; upper, X-band frequency. The crystal axes are X, Y, and Z, with Z orthogonal to the $(11\bar{1})$ face, X defined by the intersection of the $(0\bar{1}1)$ and $(\bar{1}11)$ faces, and $Y = X \times Z$.

Table I. Principal Values and Directions of g and D Tensors for $[Cu(bpt)(CF_3SO_3)(H_2O)]_2$[a]

g_{xx} = 2.055 (1)	g_{yy} = 2.051 (1)	g_{zz} = 2.232 (1)
0.6 (1)	0.6 (1)	−0.394 (4)
0.7 (1)	−0.6 (1)	0.171 (6)
0.16 (6)	0.40 (2)	0.903 (2)
$D_{x'x'}$ = 0.0026 (5)[b]	$D_{y'y'}$ = 0.0338 (3)[b]	$D_{z'z'}$ = −0.0364 (4)[b]
0.874 (3)	−0.143 (8)	−0.465 (5)
−0.070 (9)	−0.9827 (9)	0.171 (4)
0.481 (5)	0.117 (6)	0.869 (3)

[a] The directions are given by the cosines referred to the crystal axes X, Y, and Z, with Z orthogonal to the $(11\bar{1})$ face, X defined by the intersection of the $(0\bar{1}1)$ and $(\bar{1}11)$ faces, and $Y = X \times Z$. [b] cm^{-1}.

Experimental Section

Single crystals of $[Cu(bpt)(CF_3SO_3)(H_2O)]_2$[20] were obtained by slow diffusion of a methanolic solution of the ligand Hbpt and an aqueous solution of $Cu(CF_3SO_3)_2$ into each other. $[(TMDT)_2Cu_2(im)(ClO_4)_2](ClO_4)$ was obtained by the procedure previously described.[3]

EPR-suitable single crystals of $[Cu(bpt)(CF_3SO_3)(H_2O)]_2$ were oriented with a Philips PW 1100 diffractometer and were found to correspond to the observed structure[20] with developed $(11\bar{1})$ and $(\bar{1}\bar{1}1)$ faces. Single-crystal EPR spectra were recorded with a Varian E-9 spectrometer equipped with standard X- (9-GHz) and Q-band (35-GHz) facilities.

Results

The polycrystalline-powder EPR spectrum of $[Cu(bpt)(CF_3SO_3)(H_2O)]_2$ recorded at X-band frequency and 77 K is shown in Figure 1.[20] This spectrum is very similar to that recorded at room temperature,[20] the main difference being that copper hyperfine splitting is clearly resolved in the low-temperature spectrum while it is not at room temperature.

The spectrum is typical of a triplet with a very anisotropic zero-field splitting.[25] In fact, in the $\Delta M = \pm 1$ region five features are neatly resolved. The two that show a splitting into seven lines are assigned to the two fine components of $g_\parallel$, while the other three must belong to the equatorial resonances. The highest and lowest field features correspond to the two g_y fine components, and the middle one corresponds to the two g_x components, which are within-error degenerate. Reported formulas[26] for the transition

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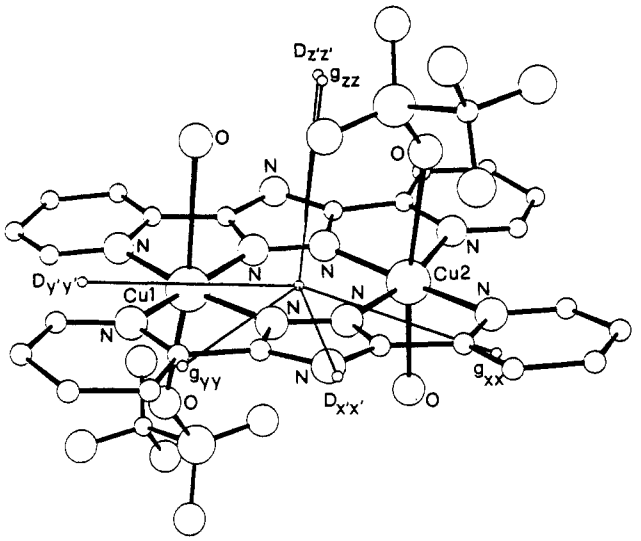

Figure 3. Sketch of $[Cu(bpt)(CF_3SO_3)(H_2O)]_2$ with the **g** and **D** tensors' principal directions.

fields along the principal axes show that a pattern like this can occur only when $E/D = 1/3$, i.e. when the rhombic splitting is maximum.[25] A first-order analysis[26] of the spectrum yields $g_z = 2.23$, $g_x = 2.06$, $g_y = 2.05$, $|D| = 0.0537$ cm^{-1}, $E/D = -1/3$, and $|A_z| = 102 \times 10^{-4}$ cm^{-1}. The assignment was confirmed through a single-crystal analysis.

Single-crystal EPR spectra were recorded at room temperature by rotating around the X, Y and Z crystal axes, with Z orthogonal to the $(11\bar{1})$ face, X defined by the intersection of the $(0\bar{1}1)$ and $(\bar{1}11)$ faces, and $Y = X \times Z$ at both X- and Q-band frequencies. The angular dependence of the transition fields in the three rotations and the best-fit curves, obtained with the procedure previously described,[27] are shown in Figure 2.

The best-fit spin-Hamiltonian parameters, together with experimental errors, are shown in Table I. The g_{zz} and $D_{z'z'}$ directions are practically parallel to each other, making an angle of 4 (1)°, while the $D_{y'y'}$ and g_{yy} axes are rotated by 51 (9)°. A sketch of the dimer with the principal axes of the **g** and **D** tensors is shown in Figure 3.

Single-crystal spectra recorded at 77 K are complicated by the presence of the hyperfine splitting, which shows evidence of large second-order effects, as will be reported elsewhere.

Discussion

The **g** tensor of $[Cu(bpt)(CF_3SO_3)(H_2O)]_2$ is in good agreement with a tetragonally elongated ligand field of four strongly interacting equatorial nitrogen atoms, plus two weak axial oxygen donors.[28] The strength of the in-plane ligand field is demonstrated by the relatively small g_{zz} value and by the very large A_{zz} value (204×10^{-4} cm^{-1} for a single copper(II) ion).

The zero-field splitting tensor **D** shows evidence of substantial exchange contributions. In fact, the largest component is not parallel to the copper–copper direction, as expected for dominant dipolar effects,[16] but to the g_{zz} direction, as was also found in a series of bis(μ-oxo)-bridged copper(II) complexes.[27,29-32] The second largest component is observed parallel to the copper–copper direction, and this result is at variance with those of other copper(II) complexes in which the magnetic orbitals lie on the same plane. In fact, in all the previous cases the smallest **D** component was found parallel to the copper–copper direction,[27-35] and this was taken as evidence of a dominant exchange mechanism involving the ground xy orbital of one ion and the excited x^2-y^2 orbital on the other ion.[29] The only other notable exception to this was found in a series of dinuclear complexes bridged by oxalato, oxamato, and oxamidato groups, where the exchange contribution to the zero-field splitting tensor was found to be very small and the largest component was parallel to the copper–copper direction.[18]

The present case, where the bridges between the two copper ions are formed by polyatomic moieties, seems to be intermediate between the two above limits: the exchange contribution to **D** is still strong enough to give a large $D_{z'z'}$ parallel to g_{zz}, but not large enough to give the pattern usual for monatomic bridges. The interpretation we gave to the exchange contribution in the μ-oxalato complexes[18] was that the polyatomic bridge is very effective in determining the antiferromagnetic coupling between the two xy magnetic orbitals,[36] but it is not effective at all in transmitting a ferromagnetic coupling between the ground xy and the excited x^2-y^2 magnetic orbitals. A confirmation of this comes from the very small magnetic coupling observed in a complex where an oxalato group bridges a copper(II) ion and an oxovanadium(IV) ion and where in fact the ground magnetic orbitals are xy and x^2-y^2, respectively.[37] In the present case the shorter copper–copper distance as compared to the oxalato-bridged case seems to suggest an intermediate situation.

The polycrystalline-powder spectra of $[Cu(bpt)(CF_3SO_3)(H_2O)]_2$ are similar to those previously reported[3] for $[(TMDT)_2Cu_2(im)(ClO_4)_2](ClO_4)$. We also recorded the spectra of the latter compound and found that they do correspond to those reported,[38-40] including some features in the 0.25-T region (Figure 1). Further, we observed at least five transitions in the intensity ratio 1:2:3:4:3 expected for the interaction of the unpaired electrons with two equivalent copper(II) ions. Therefore, we assign these features to the low-field component of g_{zz} of the triplet, the high-field component being at 0.329 T on our spectrometer. The fact that no hyperfine splitting is resolved on this feature may be due to well-documented second-order effects that make the hyperfine splitting on the two fine-structure lines of a triplet very anisotropic.[19,41,42] We then assign the second feature from low field, at 0.287 T, and the one at highest field, at 0.348 T, to g_{yy} and finally the intense feature at 0.312 T to g_{xx}, by analogy with the assignment we have confirmed with single-crystal data on $[Cu(bpt)(CF_3SO_3)(H_2O)]_2$. The spin-Hamiltonian parameters for $[(TMDT)_2Cu_2(im)(ClO_4)_2](ClO_4)$ are then obtained as $g_{xx} = 2.09$, $g_{yy} = 2.02$, $g_{zz} = 2.22$, $|D| = 399 \times 10^{-4}$ cm^{-1}, $E/D = -0.27$, and $|A_{zz}| = 100 \times 10^{-4}$ cm^{-1}, in good agreement with those of $[Cu(bpt)(CF_3SO_3)(H_2O)]_2$. In this assignment the largest zero-field splitting is parallel to g_{zz} and A_{zz}. We may then conclude that also in $[(TMDT)_2Cu_2(im)(H_2O)_2]$ the exchange contribution to **D** is relevant, since the dipolar term D^{dip} (calculated[43] by using the observed metal–metal distance and g values) should be 90×10^{-4} cm^{-1}, roughly one-fourth the observed value, and should be associated with a $g_\perp$ feature, not with g_{zz}.

Finally, we feel that we can try to assign the spectra of Cu_2-Cu_2SOD, which are redrawn in Figure 1 (after Figure 1 of ref 24). Indeed, these are characterized by broad lines[21-24] with a well resolved feature at 0.36 T, which in the literature has been used as a fingerprint of this species, and another, less characterized

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one, peaking at 0.26 T, in the low-field region. From the comparison with the spectra of $[Cu(bpt)(CF_3SO_3)(H_2O)]_2$ and $[(TMDT)_2Cu_2(im)(ClO_4)_2](ClO_4)$, we assign the 0.36-T feature to the high-field component of g_{yy}, the low-field one being at 0.26 T. This yields, in approximate terms, $g_{yy} = 2.07$ and $D_{y'y'} = 317 \times 10^{-4}$ cm^{-1}. The bumps observed at fields lower than 0.26 T should correspond to the low-field transition of g_{zz}, the high-field one being in the region obscured by mononuclear copper impurities. The large signal between 0.26 and 0.32 T must be associated with g_{xx}. If this assignment is correct, and the similarity to the now well-characterized simple copper complexes makes this rather feasible, it seems that also in Cu_2Cu_2SOD, where the interacting metal ions are at least 600 pm apart, the zero-field splitting tensor still has relevant exchange contribution, since in the hypothesis of only dipolar terms $D_{y'y'}$ could not exceed (60–70) $\times 10^{-4}$ cm^{-1}.

Acknowledgment. Thanks are due to Prof. S. J. Lippard for pointing out to us the misprint in ref 3.

Registry No. $[Cu(bpt)(CF_3SO_3)(H_2O)]_2$, 97150-35-1; $[(TMDT)_2Cu_2(im)(ClO_4)_2](ClO_4)$, 68829-54-9; Cu_2Cu_2SOD, 54651-53-5.

Contribution from the Istituto di Teoria e Struttura Elettronica e Comportamento Spettrochimico dei Composti di Coordinazione del CNR, Area della Ricerca di Roma, 00016 Monterotondo Stazione, Rome, Italy

Synthesis, X-ray Crystal Structure, and Chemical and Physical Properties of the New Linear-Chain Mixed-Valence Complex (μ-Iodo)tetrakis(dithioacetato)dinickel, $Ni_2(CH_3CS_2)_4I$, and X-ray Crystal Structure of the Precursor Tetrakis(dithioacetato)dinickel(II), $Ni_2(CH_3CS_2)_4$[†]

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Received August 28, 1984

The precursor tetrakis(dithioacetato)dinickel(II), $Ni_2(CH_3CS_2)_4$, crystallizes in the triclinic space group $P\bar{1}$ with the unit-cell dimensions $a = 9.017$ (3) Å, $b = 9.098$ (3) Å, $c = 11.272$ (4) Å, $\alpha = 105.07$ (2)°, $\beta = 67.67$ (2)°, and $\gamma = 93.44$ (2)°. The crystal structure of the complex consists of $[Ni_2S_8]$ dimeric units with a bridging acetate cage structure, in which the Ni–Ni distance is 2.564 (1) Å. The two $[NiS_4]$ squares are twisted 24° from the eclipsed geometry. Adjacent dimers in the unit cell are laterally displaced in such a way as to achieve a "slipped stack" arrangement, the nearest-neighbor contact being between sulfur and nickel. The iodine oxidative addition to the described compound gives a shining black crystalline product having the formula $Ni_2(CH_3CS_2)_4I$, where the formal oxidation number of the nickel atom is +2.5. This compound crystallizes in the monoclinic space group $P2/n$ with $a = 8.934$ (2) Å, $b = 8.382$ (2) Å, $c = 12.492$ (2) Å, and $\beta = 106.21$°. The crystal structure consists of linear chains of ---I---$[Ni_2S_8]$---I---$[Ni_2S_8]$--- stacking along the crystallographic b axis. The Ni–Ni distance in the dimer is 2.514 (3) Å, and the Ni–I distances are 2.928 (4) and 2.940 (4) Å, respectively. This is the first example, as far as we know, of a mixed-valence nickel compound, where linear chains of $[Ni_2S_8]$ chromophores, bridged through iodine, are present. The presence of a nearly symmetrical metal–iodine–metal bridge is responsible for the observed electrical conductivity, i.e. 5×10^{-6} Ω^{-1} cm^{-1}. Variable-temperature conductivity measurements show that the electrical conductivity follows an exponential temperature dependence, with an activation parameter, E_a, $\simeq$0.07 eV. A "hopping type" mechanism for the electrical conductivity is suggested.

Introduction

We recently found that several nickel-triad metal(II) derivatives of dithiocarboxylic acids, RCSSH, where R is an alkyl group, having columnar structure,[1,2] react with halogens.[3] In the case of the tetrakis(dithioacetato)diplatinum(II) complex,[2] two compounds were isolated. The first one, having the formula $Pt_2(CH_3CS_2)_4I_2$ with Pt formal oxidation state +3, is diamagnetic and consists of discrete $[Pt_2S_8I_2]$ units. The second one, having the formula $Pt_2(CH_3CS_2)_4I$, is a linear-chain mixed-valence compound, where the $[Pt_2S_8]$ units are linked by iodine atoms.[3] This compound belongs to the class of one-dimensional materials that has received considerable attention in the last few years,[4] and it is unusual because it is a semiconductor with a rather high maximum powder electrical conductivity, 7×10^{-3} Ω^{-1} cm^{-1}, at room temperature.[3,5]

With the aim of isolating new linear-chain compounds with sulfur donor ligands, we studied the reaction of the nickel and palladium analogues with halogens. Here we report the synthesis, the X-ray crystal structure, and the physical properties of the product obtained by reaction of tetrakis(dithioacetato)dinickel(II) with iodine and, for comparison, the X-ray crystal structure of the precursor tetrakis(dithioacetato)dinickel(II), $Ni_2(CH_3CS_2)_4$.

Experimental Section

Elemental analyses were performed by Alfred Bernhardt Mikroanalytische Laboratorium, Elbach, West Germany, and by Servizio Microanalisi del CNR, Area della Ricerca di Roma, Rome, Italy.

Reagents. Dithioacetic acid, CH_3CS_2H, was prepared according to known procedures.[6] $NiCl_2 \cdot 6H_2O$ was used as obtained from BDH Chemicals Ltd.

$Ni_2(CH_3CS_2)_4$. Tetrakis(dithioacetato)dinickel(II) was prepared as reported previously,[7] and the purity was checked by normal physicochemical methods. Crystals suitable for X-ray studies were grown by slow evaporation of a carbon disulfide solution of the complex. The RPE iodine was used as obtained commercially from Carlo Erba Ltd., without purification.

$Ni_2(CH_3CS_2)_4I$. $Ni_2(CH_3CS_2)_4$ (0.484 g, 1×10^{-3} mol) was dissolved in CS_2, 100 mL, and filtered, and a red-brown solution was obtained. Iodine (0.126 g, 5×10^{-4} mol) dissolved in the same solvent, 30 mL, was added dropwise to the red solution. A black, needlelike microcrystalline product immediately separated. Suitable crystals for X-ray investigations were obtained by the diffusion technique. Anal. Calcd for $C_8H_{12}S_8Ni_2I$ ($M_r = 608.88$): C, 15.78; H, 1.97; S, 42.12; Ni, 19.29; I, 20.84. Found: C, 15.76; H, 1.90; S, 42.01; Ni, 19.09; I, 21.02.

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