Synthesis, Crystal and Molecular Structure of Tetraphenylarsonium Bis(maleonitriledithiolato)tellurate(II), $[AsPh_4]_2[Te(mnt)_2]$,† and Single-crystal Electron Spin Resonance Spectra of the System $[AsPh_4]_2[Cu/Te(mnt)_2]$

Ljubo Golič *
Department of Chemistry, Edvard Kardelj University, 61000 Ljubljana, Yugoslavia
Wolfgang Dietzsch, Klaus Köhler, Joachim Stach, and Reinhard Kirmse
Sektion Chemie, Karl-Marx-Universität, 7010 Leipzig, Talstrasse 35, German Democratic Republic

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The crystal and molecular structure of bis(tetraphenylarsonium) bis(maleonitriledithiolato)tellurate(II), a new tellurium(II) compound containing dithiolene ligands, and the single-crystal e.s.r. spectra of the system $[AsPh_4]_2[^{63}Cu/Te(mnt)_2]$ are reported. $[AsPh_4]_2[Te(mnt)_2]$ crystallises in the triclinic space group $P\bar{1}$, with $a = 10.211(2)$, $b = 14.460(2)$ Å, $c = 18.583(3)$ Å, $\alpha = 105.95(2)$, $\beta = 95.60(2)$, $\gamma = 77.67(2)$°, and $Z = 2$; $R = 0.047$ for 7 749 observed reflections. The tellurium atoms have trapezoid planar co-ordination with Te–S bond distances of 2.501(1), 2.482(2), 2.971(2), and 3.104(2) Å. In the single-crystal e.s.r. spectra the signals of two Cu sites with somewhat different spin-Hamiltonian parameter sets are observed. The $\tilde{g}$ and the ^{63}Cu hyperfine tensors are rhombic symmetric. The planar $[Cu(mnt)_2]^{2-}$ anions are considerably distorted but do not adopt the structure of the tellurium host.

The structural analysis of $[AsPh_4]_2[Te(mnt)_2]$ [mnt = maleonitriledithiolate, $^{-}SC(CN){=}C(CN)S^{-}$] reported here is part of a study on the influence of diamagnetic host lattices upon the e.s.r. and ENDOR (electron nuclear double resonance) parameters of the paramagnetic $[Cu(mnt)_2]^{2-}$ system in single-crystal experiments. Until now the originally planar copper(II) chelate was investigated in the hosts $[NBu_4]_2[Ni(mnt)_2]$,[1,2] having a planar co-ordination sphere, and $[AsPh_4]_2[Zn(mnt)_2]$[3] with a nearly tetrahedral ZnS_4 arrangement (the torsion angle between the chelate rings was found to be 84°). Because of the presence of lone pairs on tellurium(II) for $[Te(mnt)_2]^{2-}$ a quite different co-ordination sphere was expected.

Hitherto no studies have been made concerning the co-ordination of the central ion Te^{II} with unsaturated 1,2-dithiolate ligands (dithiolenes) but many *X*-ray structure analyses of complexes with 1,1-dichalcogeno ligands have been published revealing interesting aspects of co-ordination possibilities.[4] Ligands such as *O,O′*-dimethyl and *O,O′*-diethyl dithiophosphates[5,6] and diethylthioselenophosphinate[7] form bis-complexes with a distorted square-planar co-ordination geometry as a part of a polymeric network where the Te^{II} ions are strongly bonded to two chalcogen donor atoms in the molecule proper and weakly to two sulphur atoms belonging to two different neighbouring molecules (according to Husebye's notation:[8,9] class II).

Ligands with stronger donor capacity, however, *e.g.* xanthates (dithiocarbonates)[8,10,11] or dithiocarbamates,[12–14] form essentially monomeric molecules where the central tellurium ions are bonded to all four sulphur atoms in the molecule with a trapezoid planar configuration. In all these cases a slight tendency towards planar five-co-ordination has been observed forming symmetrically related pairs of molecules with two weak intermolecular Te–S bonds (3.5—3.7 Å) (according to Husebye's notation:[8,9] class I).

A third co-ordination type was found in the anion of tetraethylammonium tris(*O*-ethyl dithiocarbonato)tellurate(II).[15] Here the tellurium ion is surrounded by five sulphur atoms at each corner of a planar pentagon with different Te–S distances.

Finally a further co-ordination geometry of Te^{II} exists in the bis-chelate with bis(diphenylthiophosphinoyl)amide, a ligand causing six-membered chelate rings.[16] For $Te[N(Ph_2PS)_2]_2$ also a planar, but centrosymmetric TeS_4 unit is reported (class V according to Husebye's notation). Thus the question arose if Te^{II} dithiolene complexes containing five-membered chelate rings resemble in their stereochemistry the corresponding complex types with geminal ligands (*e.g.* dithiocarbamates) or class I or class V, since the bite angle of dithiolene ligands should be between the angles measured for these ligand types.

Experimental

Preparation of $[AsPh_4]_2[Te(mnt)_2]$.—$Na_2[Te(S_2O_3)_2]\cdot 2H_2O$[17] (0.868 g, 2 mmol) dissolved in water–methanol (1:1 v/v, 40 cm^3) was allowed to react slowly with a mixture of $Na_2(mnt)$[18] (0.744 g, 4 mmol) and $AsPh_4Cl$ (1.675 g, 4 mmol) in methanol (40 cm^3). From the dark brown solution black shiny crystals were deposited. The raw product was filtered off, washed with water followed by propan-2-ol and diethyl ether, and dried *in vacuo*. The complex salt was recrystallised by dissolving in acetone and slowly reducing the solvent *in vacuo* without heating. Yield: 1.4 g (60%), m.p. 164—165 °C (Found: C, 57.35; H, 3.30; N, 4.75; S, 10.55. Calc. for $C_{56}H_{40}As_2N_4S_4Te$: C, 57.25; H, 3.35; N, 4.75; S, 10.90%).

X-Ray Crystal Structure of $[AsPh_4]_2[Te(mnt)_2]$.—Crystals suitable for diffraction studies were grown from a pyridine solution of the complex salt covered with a layer of ethanol and stored at 0 °C over 24 h. A crystal of size 0.6 × 0.5 × 0.4 mm was used for the diffraction studies.

Crystal data. $C_{56}H_{40}As_2N_4S_4Te$, $M = 1\,174.66$, triclinic, space group $P\bar{1}$, $a = 10.211(2)$, $b = 14.460(2)$, $c = 18.583(3)$ Å, $\alpha = 105.95(2)$, $\beta = 95.60(2)$, $\gamma = 77.67(2)$°, $U = 2\,575(5)$ Å^3, $D_c = 1.515$ g cm^{-3}, D_m not measured, $Z = 2$, Mo-K_α radiation, $\lambda = 0.710\,69$ Å, $\mu = 2.046$ mm^{-1}, $F(000) = 1\,172$, $T = 293(1)$ K.

Structure determination and refinement. Data were collected with a CAD-4 diffractometer using graphite-monochromated Mo-K_α radiation. Lattice parameters were determined from settings and least-squares refinement of 90 reflections with $10 < \theta < 12°$. A total of 12 399 reflections with $\theta \leqslant 28°$ and

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1988, Issue 1, pp. xvii—xx.

Table 1. Final fractional co-ordinates ($\times 10^4$) for $[Te(mnt)_2]^{2-}$ with estimated standard deviations in parentheses

Atom	x	y	z
Te	4 253.2(3)	9 035.8(2)	1 756.3(2)
S(1)	2 475(1)	8 357(1)	856(1)
S(2)	4 692(1)	6 803(1)	1 619(1)
C(1)	2 059(5)	7 571(3)	1 333(3)
C(2)	2 984(5)	6 932(3)	1 628(3)
C(3)	651(6)	7 623(4)	1 377(3)
C(4)	2 491(7)	6 321(4)	1 991(3)
N(1)	−482(6)	7 679(7)	1 384(4)
N(2)	2 117(8)	5 845(5)	2 303(4)
S(3)	3 202(1)	10 643(1)	1 511(1)
S(4)	5 401(1)	10 519(1)	2 938(1)
C(5)	2 967(5)	11 388(3)	2 426(3)
C(6)	3 878(5)	11 329(3)	3 002(3)
C(7)	1 747(6)	12 100(4)	2 541(4)
C(8)	3 524(7)	11 939(4)	3 731(4)
N(3)	769(7)	12 680(5)	2 621(4)
N(4)	3 267(8)	12 393(4)	4 329(4)

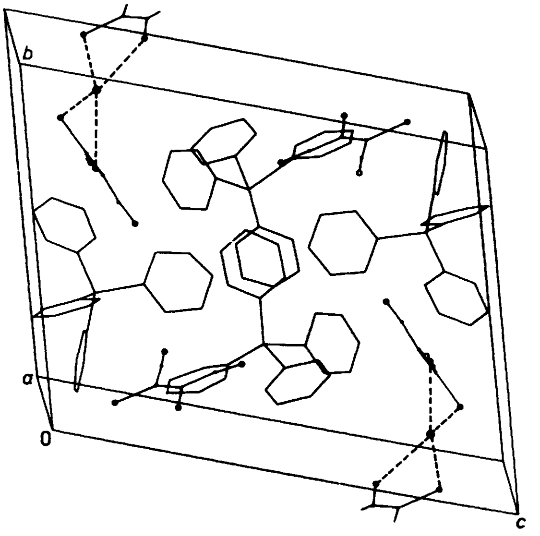

Figure 1. Unit-cell packing of $[AsPh_4]_2[Te(mnt)_2]$

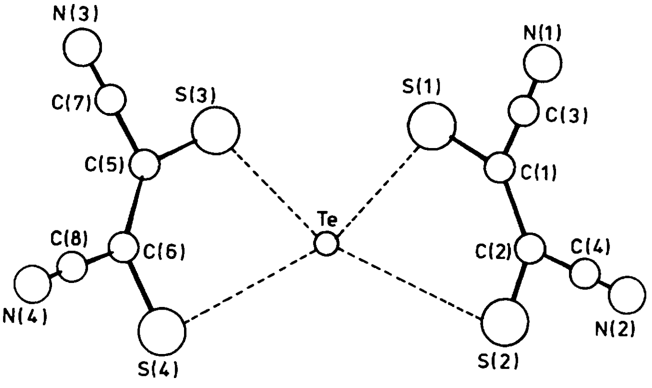

Figure 2. Atomic numbering and view of the structure of the $[Te(mnt)_2]^{2-}$ anion showing the trapezoidic arrangement of the sulphur atoms

$l \geqslant 0$ were collected using a ω—2θ scan, scan width ($0.7 + 0.3\tan\theta$)°, 25% on each side used for background measurement, horizontal aperture ($2.4 + 0.9\tan\theta$) mm, vertical aperture 4 mm, and maximum scan time 40 s. Three standard reflections were measured after each 192 reflections, 4% decay; 4 650 reflections had intensities less than 4.0 $\sigma(I)$ and were taken as unobserved. An absorption correction[19] based on crystal shape was applied with a minimum transmission factor of 0.26 for the 001 reflection and a maximum value of 0.48 for the $1\bar{2}3$ reflection. The structure was solved from a Patterson map and refined minimising $\Sigma w(|F_o| - |F_c|)^2$ to R and R' values of 0.047 and 0.063 respectively. All non-hydrogen atoms refined with anisotropic thermal parameters. Positions of the hydrogen atoms were calculated and were included as fixed atom contributions in the refinement. An empirical weighting function $w = W_f x W_s$ where $W_f(|F_o| < 12.0) = |F_o|/12.0$, $W_f(|F_o| > 13.0) = 13.0/|F_o|^{1.2}$, $W_f(12.0 < |F_o| < 13.0) = 1.0$ and $W_s(\sin\theta < 0.47) = (\sin\theta/0.47)^{1.5}$, $W_s(\sin > 0.47) = 1.0$ was applied in order to keep $\Sigma w(\Delta F)^2$ uniform over the ranges of $\sin\theta/\lambda$ and $|F_o|$. In the final refinement cycle there were 10 624 contributing reflections (m) [including those with $I/\sigma(I) < 4.0$ for which F_c exceeded F_o], 604 variables (n), $m/n = 17.6$, $S = [\Sigma w(\Delta F)_2/(m - n)]^{\frac{1}{2}} = 0.82$, ratio of maximum shift to error 1.4 at scale factor, average ratio 0.061, maximum and minimum values in final difference map 2.1 e Å^{-3} (0.60 Å to Te atom) and 2.0 e Å^{-3} (0.97 Å to Te atom). Atomic scattering and dispersion factors for neutral Te, As, S, N, C,[20,21] and H[22] atoms were used. A DEC-10 computer at the University Computer Centre Ljubljana and the *X*-RAY 76 system[23] of crystallographic programs were used for all calculations.

E.S.R. Spectra.—Suitable single crystals of $[AsPh_4]_2[Te(mnt)_2]$ doped with $[AsPh_4]_2[^{63}Cu(mnt)_2]$ (^{63}Cu enrichment: 97.8%) were grown according to those for the diffraction studies and by adding 0.5—3.0 mol% of the Cu complex to the solution. The actual Cu^{2+} concentration in the crystals (relative to Te^{2+}) was estimated from a signal intensity measurement and found to be only ≈0.1%.

Single-crystal e.s.r. spectra were recorded at $T = 295$ K with a Varian E-112 spectrometer in three perpendicular planes every 5 or 10° depending on their complexity. The principal values of the $\tilde{g}$ and the ^{63}Cu hyperfine tensor $\tilde{A}^{Cu}$ were obtained using standard computer programs.[2] Calculations were performed with a Robotron R40 computer.

Results and Discussion

Crystal Structure.—The atomic co-ordinates are listed in Table 1. The structure consists of tetraphenylarsonium cations and bis(maleonitriledithiolato)tellurate(II) anions. The unit-cell contents are shown in Figure 1.

The geometry of the cations compares satisfactorily with that reported[3] for a number of tetraphenylarsonium salts. Mean As–C distances of 1.911(5) and 1.903(2) Å are observed for the two different cations with mean C–As–C angles of 109.5(17) and 109.5(31)°. The phenyl rings show small deviations from their known geometry.

The main feature of the structure is the bis(maleonitriledithiolato)tellurate(II) anion, shown in Figures 2 and 3 together with the atomic numbering. The tellurium atom has trapezoid planar four-co-ordination with no intermolecular contacts. With two short Te–S bond lengths of 2.482(2) and 2.501(1) Å at an interbond angle of 86.29(5)° and two long ones of 2.971(2) and 3.104(2) Å at an interbond angle of 126.70(5)° the anion belongs formally to class I Te^{II} complexes. Intraligand angles of 72.17(4) and 74.41(5)° correspond to S–S bites of 3.337(2) and 3.321(2) Å, longer than the values found in carbamate and xanthate complexes of Te^{II} with almost equal co-ordination and

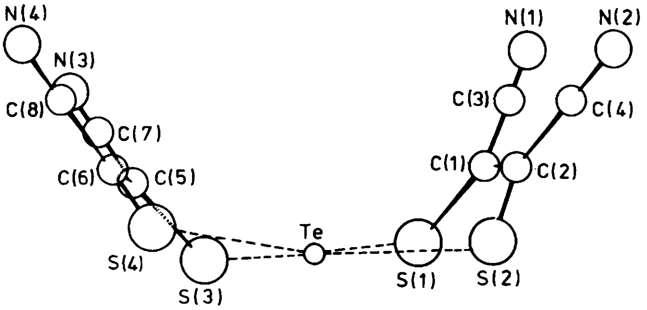

Figure 3. View of the $[Te(mnt)_2]^{2-}$ anion showing the 'boat conformation' arrangement of the ligands

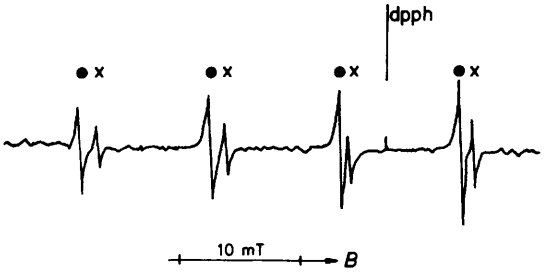

Figure 4. Typical single-crystal X-band e.s.r. spectrum of $[AsPh_4]_2[^{63}Cu/Te(mnt)_2]$: $T = 295$ K, ● site A, × site B; dpph = diphenylpicrylhydrazyl

Table 2. Bond lengths (Å) and angles (°) for $[Te(mnt)_2]^{2-}$

Te–S(1)	2.501(1)	S(1)–Te–S(3)	86.29(5)
Te–S(2)	3.104(2)	S(1)–Te–S(2)	72.17(4)
Te–S(3)	2.482(2)	S(3)–Te–S(4)	74.41(5)
Te–S(4)	2.971(2)	S(2)–Te–S(4)	126.70(5)
C(1)–S(1)	1.759(6)	S(1)–C(1)–C(2)	123.6(4)
C(2)–S(2)	1.715(5)	S(2)–C(2)–C(1)	125.7(5)
C(1)–C(2)	1.361(7)	S(1)–C(1)–C(3)	115.3(4)
C(1)–C(3)	1.433(8)	S(2)–C(2)–C(4)	116.9(4)
C(2)–C(4)	1.441(9)	C(2)–C(1)–C(3)	121.1(6)
C(3)–N(1)	1.143(9)	C(1)–C(2)–C(4)	117.4(5)
C(4)–N(2)	1.153(11)	C(1)–C(3)–N(1)	117.0(8)
		C(2)–C(4)–N(2)	117.8(6)
C(5)–S(3)	1.753(5)	S(3)–C(5)–C(6)	123.6(4)
C(6)–S(4)	1.728(5)	S(4)–C(6)–C(5)	125.0(4)
C(5)–C(6)	1.357(8)	S(3)–C(5)–C(7)	116.1(4)
C(5)–C(7)	1.428(7)	S(4)–C(6)–C(8)	116.9(4)
C(6)–C(8)	1.429(8)	C(6)–C(5)–C(7)	120.3(5)
C(7)–N(3)	1.151(8)	C(5)–C(6)–C(8)	117.9(5)
C(8)–N(4)	1.148(9)	C(5)–C(7)–N(3)	178.5(8)
		C(6)–C(8)–N(4)	176.8(7)

smaller than 3.67 or 3.77 Å found in di[bis(diphenylthiophosphinoyl)amido-*S,S'*]tellurium(II).[16] The TeS_4 group is roughly planar. The distances from the least-squares plane through tellurium and the four ligand sulphur atoms are −0.141, 0.186, −0.058, −0.124, and 0.128 Å for Te, S(1), S(2), S(3), and S(4), respectively.

The two maleonitriledithiolate ligands are planar, with deviations from the best plane of less than 0.018 and 0.072 Å. They form dihedral angles with the best plane through the TeS_4 group of 59.5(2) and 52.2(3)°. The tellurium atom lies 1.77(1) and −1.63(1) Å out of these planes. Both ligands form an angle of 74.6(2)° to each other producing a boat conformation. The bond lengths and angles of the ligands are presented in Table 2. The longer lengths S(1)–C(1) and S(3)–C(5) of 1.759(6) and 1.753(5) Å correspond to the short Te–S bonds, whereas the shorter S(2)–C(2) and S(4)–C(6) lengths of 1.715(5) and 1.728(5) Å correspond to the longer Te–S bonds. However, they are not short enough to indicate significant double-bond character.

E.S.R. Spectra.—For a general orientation of magnetic field in single-crystal e.s.r. spectra the signals of two magnetically non-equivalent sites (later designated sites A and B) are observed. This is unexpected because according to the crystal structure of the tellurium host complex in the single-crystal spectra only the signals of one site should be observed: the two $[Te(mnt)_2]^{2-}$ anions in the unit cell are structurally equivalent. However, it is interesting to note that the angular dependences of the spectra of sites A and B are very close to each other indicating only small differences in the spin-Hamiltonian parameters of both sites. A typical spectrum is shown in Figure 4.

The spectra were analysed using the spin-Hamiltonian (1),

$$\hat{H}_{sp} = \mu_B\vec{B}\cdot\bar{g}\cdot\vec{S} + \vec{S}\cdot\bar{A}^{Cu}\cdot\vec{I}^{Cu} \qquad (1)$$

where $S = \frac{1}{2}$ and $I^{Cu} = \frac{3}{2}$. The program used calculates transition energies and minimises the error function (2), where N is

$$h\left[\frac{1}{N}\sum_i^N(\nu^i_{obs.} - \nu^i_{calc.})^2\right]^{\frac{1}{2}} \qquad (2)$$

the number of peaks in the e.s.r. spectrum by varying the tensor elements of the Hamiltonian (1). In (2) the summation index i runs over all e.s.r. peaks, from $i = 1$ to N, in the spectra of the same site. In the analysis ^{63}Cu quadrupole interactions have been neglected since for these purposes the determination of the line positions was not accurate enough due to overlapping of the signals of site A with those of site B. The principal values of $\bar{g}$ and $\bar{A}^{Cu}$ obtained for both sites are listed in Table 3 and therein compared with the parameters reported for $[Cu(mnt)_2]^{2-}$ incorporated in completely different host lattices: the planar $[Ni(mnt)_2]^{2-}$ [1,2] and the tetrahedrally co-ordinated $[Zn(mnt)_2]^{2-}$.[3]

The e.s.r. parameters obtained for the $[Cu/Te(mnt)_2]^{2-}$ system differ considerably from those of the planar $[Cu/Ni(mnt)_2]^{2-}$ system: (*a*) the anisotropy of the ^{63}Cu hyperfine tensor $\bar{A}^{Cu}$ in the A_1^{Cu}, A_2^{Cu} plane is much larger for $[Cu/Te(mnt)_2]^{2-}$, A_3^{Cu} appears to be reduced, and (*b*) the maximum component of the $\bar{g}$ tensor is found to be remarkably larger than that observed for $[Cu/Ni(mnt)_2]^{2-}$. Furthermore, and in contrast to the $[Cu/Ni(mnt)_2]^{2-}$ system, non-coincidence has been found for the principal axes of the small components of $\bar{g}$ and $\bar{A}^{Cu}$ of both sites in the tellurium host [the angle between the directions of g_1 and A_1^{Cu} (and g_2, A_2^{Cu}) was determined to be 6° for site A and 4° for site B]. The directions of g_3 and A_3^{Cu} are found to be coincident. These results indicate that the $[Cu(mnt)_2]^{2-}$ anions will be considerably distorted if incorporated in the $[AsPh_4]_2[Te(mnt)_2]$ host complex: the Cu atom no longer occupies an inversion centre as found for the $[Cu/Ni(mnt)_2]^{2-}$ system; the increased anisotropy in the plane spanned by g_1, g_2; A_1^{Cu}, A_2^{Cu} and the observed non-coincidence between these prinicipal axes reflects a noticeable influence of the trapezoid planar TeS_4 unit.

The presence of two sites with somewhat different e.s.r. parameters and with closely related directions of the principal axes of $\bar{g}$ and $\bar{A}^{Cu}$ (Figure 5 shows angles between corresponding principal axes of the $\bar{g}$ tensors of both sites) seems to be caused

Table 3. Principal values of the g and ^{63}Cu hyperfine tensor A^{Cu} of $[Cu(mnt)_2]^{2-}$ in different host complexes (A_i^{Cu} in 10^{-4} cm^{-1})

	$[AsPh_4]_2[Te(mnt)_2]$[a]			
	Site A	Site B	$[NBu^n{}_4]_2[Ni(mnt)_2]$[b]	$[AsPh_4]_2[Zn(mnt)_2]$[c]
g_1	2.023	2.022	2.023	2.017
g_2	2.029	2.028	2.026	2.024
g_3	2.105	2.099	2.086	2.089
g_{av}[d]	2.052	2.050	2.045	2.043
A_1^{Cu}	28.3	31.4	41.4	13.5
A_2^{Cu}	46.9	47.9	40.4	20.5
A_3^{Cu}	145.5	150.9	161.1	110.0
A_{av}^{Cu}[d]	73.6	76.7	81.0	48.0

[a] Experimental errors: $g_i \pm 0.001$, $A_i^{Cu} \pm 1.0$ cm^{-1}. [b] Data taken from ref. 2. [c] An angle of $\approx 30°$ between the two ligand planes was found for the incorporated $[Cu(mnt)_2]^{2-}$ anion; data taken from ref. 3. [d] $g_{av} = (g_1 + g_2 + g_3)/3$, $A_{av}^{Cu} = (A_1^{Cu} + A_2^{Cu} + A_3^{Cu})/3$.

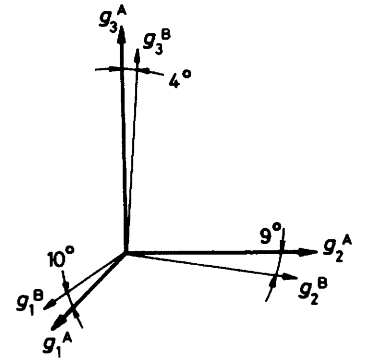

Figure 5. Relative orientations of the principal axes of the $\bar{g}$ tensor of sites A and B to each other

by difficulties arising upon incorporation of the $[Cu(mnt)_2]^{2-}$ anions into the host lattice which has a totally different structure. This agrees with the fact that in all attempts made to prepare single crystals the actual concentration of $[Cu(mnt)_2]^{2-}$ with respect to $[Te(mnt)_2]^{2-}$ does not exceed 0.1% although the Cu:Te ratio used was varied from 0.5:100 to 3:100. The observation of two closely related sites in the e.s.r. spectra suggests the presence of two favoured incorporation positions for the $[Cu(mnt)_2]^{2-}$ anions. However, as indicated by the intensity ratio of the signals observed for both sites I(site A):I(site B) $\approx$ 2:1 (see Figure 4), site A appears to be energetically more stabilized.

For the $[Cu/Ni(mnt)_2]^{2-}$ and $[Cu/Zn(mnt)_2]^{2-}$ systems the actual structure of the Cu complex in the host could be determined by means of ^{33}S (e.s.r.) and ^{13}C (ENDOR) data.[1–3] In the present case, however, because of the unsatisfactory signal-to-noise ratio these interactions could not be studied considering the very low natural abundance of the nuclei ^{33}S and ^{13}C. Therefore, an exact determination of the actual structures of sites A and B is not possible. Extended-Hückel molecular orbital calculations made using the structure of the host complex could not reproduce the e.s.r. parameters observed but support 'in-between' structures for the incorporated $[Cu(mnt)_2]^{2-}$ anions with g_3, A_3^{Cu} directed perpendicular to the TeS_4 plane.

Acknowledgements

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