Ligand Exchange Reactions between Copper(II) and Nickel(II) Chelates of Different Sulphur and Selenium Containing Ligands.
VII*. Single-crystal ESR Study on the Mixed Ligand Chelate System Ph4As[Cu/Zn(mnt)(Et2dtc)] and Crystal and Molecular Structure of Ph4As-[Zn(mnt)(Et2dtc)]**

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Abstract

The synthesis and crystal and molecular structure of the first zinc(II) mixed ligand chelate containing a dithiolene ligand (maleonitriledithiolate) and N,N-diethyldithiocarbamate are reported. The compound Ph4As[Zn(mnt)(Et2dtc)] crystallizes monoclinic, space group $P2_1/c$ with four molecules in the unit cell; $a = 17.834(3)$, $b = 12.056(2)$, $c = 16.171(4)$ Å, $\beta = 93.73(2)°$.

The coordination geometry of the ZnS_4 unit is nearly tetrahedral, with a dihedral angle of 87.6° between the chelate rings. The structure is compared with those of both the parent compounds (Ph4As)2[Zn(mnt)2] and Zn2(Et2dtc)4. Ph4As[Zn(mnt)(Et2dtc)] could be used as the host lattice in single-crystal ESR investigations of the planar Cu mixed ligand complex. The rhombic spin-Hamiltonian parameters g and A^{Cu} are indicative of a low symmetry of the incorporated [Cu(mnt)(Et2dtc)]⁻ complex anions. In order to substantiate the experimental findings about the actual structure of the copper molecules, the principal values of g and A^{Cu} were recalculated by means of Extended Hückel MO calculations. However, the calculations performed for the dihedral angles between the ligand planes varying between 0° and 90° suggest that the rotation of the ligands is not larger than 10°

Introduction

The ligand exchange behaviour of Cu(II) and Ni(II) chelates of unsaturated geminal and vicinal sulphur and/or selenium ligands has been investigated in detail and well classified [2, 3]. For synthetic work the most important fact is that the mixed ligand chelates are obtained quantitatively if four-membered chelate rings and five-membered chelate rings are combined. However, up to now, unambiguous evidence for planar transition metal complexes was given only by ESR spectroscopy and, in a few cases, by X-ray structure analyses [4–10]. In this work we show that chelates of the d^{10} metal ion Zn(II) despite their tetrahedral coordination geometry, obey the same exchange rules; this means that, e.g., the bis(maleonitriledithiolato)zincate(II) anion, [Zn(mnt)2]²⁻, and zinc(II)-bis(N,N-diethyldithiocarbamate), Zn(Et2dtc)2, react quantitatively in suitable solvents to give the mixed ligand chelate [Zn(mnt)(Et2dtc)]⁻ (1).

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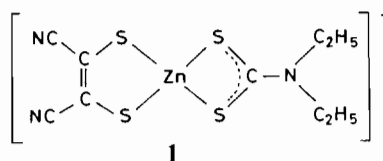
Some single-crystal ESR or ENDOR studies on Cu(II) or Ni(III) mixed ligand species were made in host lattices of the planar Ni(II) chelates, which are as a rule isostructural with the Cu(II) chelates [8, 9, 11, 12]. For the three single-crystal systems Cu/Zn-(Et2dtc)2 [14], Cu/Zn(Et2dsc)2 [14c] (Et2dsc =

N,N-diethyldiselenocarbamate) and $(Ph_4As)_2[Cu/Zn(mnt)_2]$ [15], it was shown that the copper guest complex, itself almost planar, partially accepts the symmetry of the tetrahedral zinc host complex. Unfortunately, the degree of distortion of the coordination sphere of the copper complex, e.g., the exact dihedral angle between both the ligand planes, is in most cases not accessible by the ESR experiment without additional calculations.

Experimental

Preparation of Compounds and Single-crystals

The parent chelates $(Ph_4As)_2[Zn(mnt)_2]$ and $Zn(Et_2dtc)_2$, necessary for synthesis of the mixed ligand chelate $Ph_4As[Zn(mnt)(Et_2dtc)]$, were prepared by standard literature methods [15, 16]. The mixed ligand compound was obtained by refluxing equimolar amounts of the starting complexes in an acetone/chloroform mixture (1:1) for 5 h. The reaction solution was reduced *in vacuo*, and the expected complex salt was precipitated using isopropanol. The compound can be recrystallized by dissolving in acetone and deposition by isopropanol; melting point 170–172 °C. *Anal.* Calc. for $C_{33}H_{30}$-N_3S_4AsZn: C, 53.7; H, 4.1; N, 5.7; S, 17.4; Zn, 8.9. Found: C, 53.7; H, 4.1; N, 5.4; S, 16.8; Zn, 8.8%. Conductivity, CH_3NO_2, 10^{-3} M, 20 °C, 89 Ω^{-1} cm^2 M^{-1}.

The corresponding Cu(II) mixed ligand complex $[Cu(mnt)(Et_2dtc)]^-$ is obtained in a similar manner as described in ref. 2. In contrast to the Ni(II) or Zn(II) complexes, $[Cu(mnt)_2]^{2-}$ and $Cu(Et_2dtc)_2$ react very fast [1].

Suitable single-crystals of $Ph_4As[Zn(mnt)(Et_2$-$dtc)]$ doped with the Cu(II) chelate can be grown by slow evaporation of an acetone/ethanol solution (ratio 10:1) containing the diamagnetic host and approx. 1% of $Ph_4As[Cu(mnt)(Et_2dtc)]$. Crystals for the X-ray structure analysis of $Ph_4As[Zn(mnt)$-$(Et_2dtc)]$ were prepared in the same manner without copper.

Crystal Data, Intensity Data, Structure Determination and Refinement

Crystals of $Ph_4As[Zn(mnt)(Et_2dtc)]$ are monoclinic, space group $P2_1/c$, $M_r = 737.17$, $a = 17.834(3)$, $b = 12.056(2)$, $c = 16.171(4)$ Å, $\beta = 93.73(2)°$, $U = 3469.5$ Å^3, $Z = 4$, $D_x = 1.411$ g cm^{-3}, at $T = 293(1)$ K. A yellow crystal of prismatic shape with dimensions $0.3 \times 0.3 \times 0.25$ mm was used for data collection. An Enraf-Nonius CAD-4 automatic diffractometer with Mo $K\alpha$ was employed. No crystal decay was observed. 5390 independent reflections, $\theta < 25°$, 2216 with $I > 3\sigma(I)$. Absorption was ignored. The Zn, As and S atoms were found by applying MULTAN 80 [13a]. A subsequent difference elec-

tron-density map revealed the remaining atoms. Refinement by full-matrix least-squares converged to conventional R and R_w values of 0.066 and 0.067, respectively. H atoms were included at calculated positions. The atomic scattering factors and anomalous dispersion corrections were taken from International Tables for X-ray Crystallography [13b]. Crystallographic calculations were performed on the DED 1091 computer at RCU Ljubljana with SHELX76 system of Computer programmes [13c]. Tables of atomic coordinates, temperature factors and F_o/F_c values have been deposited with the Editor-in-Chief as Supplementary Data and are available on request. Atomic coordinates have also been submitted to the Crystallographic Data Centre, Cambridge, U.K.

ESR Spectra

The single-crystal ESR spectra were recorded at room temperature using an E-112 spectrometer (VARIAN) in the X-band. The tensor parameters of the spin-Hamiltonian were obtained by studying the angular dependence of the ESR spectra in three different planes.

Results and Discussion

Structure of the Complex Salt

As shown in Fig. 1, the unit cell contains four molecules. The most important interatomic distances and angles of the complex anion with their estimated standard deviations are collected in Table 1. The structure of the tetraphenylarsonium cation is in good agreement with earlier determinations and is not further discussed.

The geometry of the ZnS_4 unit is almost tetrahedral, like that found for the starting complex $[Zn(mnt)_2]^{2-}$ [15] and in contrast to the coordination geometry of the other starting complex Zn-$(Et_2dtc)_2$. Dithiocarbamato complexes of Zn(II) consist of dimeric molecules $Zn_2(R_2dtc)_4$ [17–19] in which one dithiocarbamate ligand is bound wholly to each zinc atom; the remaining two ligands of such a unit act as links between two zinc atoms, causing a rather distorted tetrahedral ZnS_4 arrangement. However, the coordination geometry can also be considered as a strong distorted trigonal bipyramidal ZnS_5 unit. As can be seen from Fig. 1, $Ph_4As[Zn$-$(mnt)(Et_2dtc)]$ crystallizes with monomeric anions.

Comparing the structures of the parent chelates and that of the mixed ligand compound, the most interesting findings are the clearly shortened Zn–S distances in the mnt part of the molecule ($[Zn$-$(mnt)_2]^{2-}$: 2.333(2) Å; $[Zn(mnt)(Et_2dtc)]^-$: 2.294(5) Å). Surprisingly, such changes were also found in all investigated nearly-planar mixed ligand systems which contained four-membered and five-
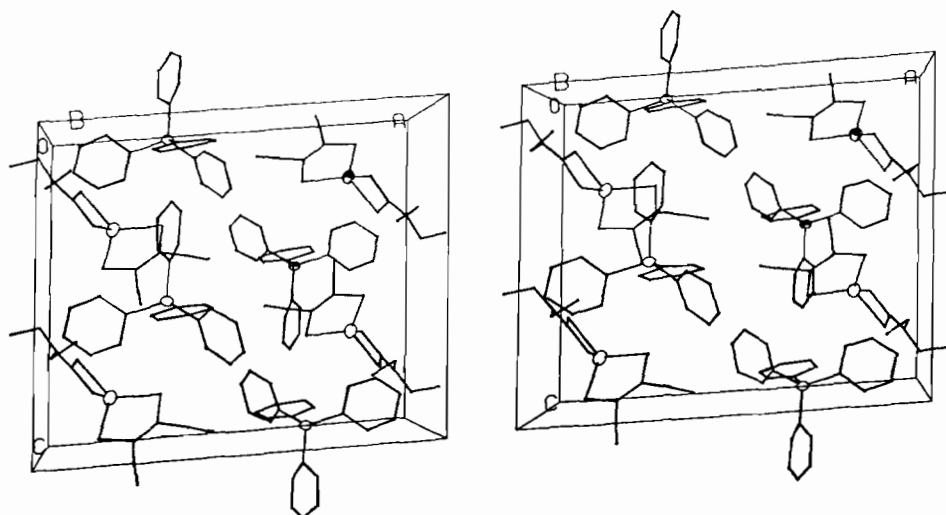
Fig. 1. Stereo-view of the unit cell of Ph₄As[Zn(mnt)(Et₂dtc)].

TABLE I. Selected Bond Lengths (A) and Angles (°) for [Zn-(mnt)(Et₂dtc)]⁻

Zn–S1	2.298(5)
Zn–S2	2.290(5)
Zn–S3	2.345(5)
Zn–S4	2.380(5)
S1–C2	1.753(16)
S2–C3	1.71(2)
S3–C5	1.730(15)
S4–C5	1.730(15)
N1–C1	1.13(3)
N2–C4	1.17(2)
N3–C5	1.285(19)
N3–C51	1.48(2)
N3–C61	1.49(2)
C2–C3	1.33(3)
C1–C2	1.44(2)
C3–C4	1.45(2)
C51–C52	1.51(3)
C61–C62	1.49(3)
S2–Zn–S1	95.8(2)
S4–Zn–S1	120.2(2)
S4–Zn–S2	120.3(2)
S3–Zn–S1	125.7(2)
S3–Zn–S2	120.4(2)
S4–Zn–S3	77.0(2)
C1–C2–S1	113.2(12)
C2–C3–S2	127.9(13)
C3–C2–S1	125.3(13)
C4–C3–S2	113.7(14)
S4–C5–S3	116.8(8)
N3–C5–S4	120.7(12)
N3–C5–S3	122.5(12)
C3–C4–N2	177.0(19)
C2–C1–N1	177.9(19)
C61–N3–C5	120.5(14)
C51–N3–C5	123.1(13)
C52–C51–N3	113.2(14)
C62–C61–N3	110.5(15)
C3–C2–C1	121.5(15)
C4–C3–C2	118.3(17)

membered chelate rings formed by unsaturated dichalcogeno ligands, e.g. Bu₄N[Cu(mnt)(Bu₂dtc)] [6, 20] (Bu₂dtc = N,N-dibutyldithiocarbamate), Bu₄N-[Ni(mnt)(Et₂dsc)] [8] (Et₂dsc = N,N-diethyldiselenocarbamate), and Bu₄N[Ni(mnt)(Et(H)dtp]·0.7acetone [9] (Et(H)dtp = ethyldithiophosphate). In the structure of both of the latter mixed ligand complexes longer M–S distances in the four-membered chelate ring were found, but such a lengthening could not be observed in [Cu(mnt)(Bu₂-dtc)]⁻ and [Zn(mnt)(Et₂dtc)]⁻. Another interesting feature in the dtc part of the zinc compound is a very small difference between the two Zn–S bonds. In the structures of Zn₂(R₂dtc)₄, these differences are 0.088(3) (R = Et), 0.096(6) (R = Me), or 0.150(3) Å (R₂ = pyrrolidine), respectively, in the comparable ligand, the sulphur atoms of which are bound to the same Zn atom. In the structure under study, this difference is reduced to 0.026(5) Å.

The dihedral angle 87.6° between the two chelate planes in the mixed ligand compound corresponds to a tetrahedral configuration, such as that found in [Zn(mnt)₂]²⁻ (83.9°). All other distances and angles show no significant deviations from those in the starting complexes.

ESR Investigations

In accordance with the crystal structure of Ph₄As-[Zn(mnt)(Et₂dtc)] the ESR spectra of the system Ph₄As[Cu/Zn(mnt)(Et₂dtc)] show the signals of two magnetically nonequivalent copper(II) molecules. The two sites in the host lattice are related by the *b*-axis. Therefore, the two sets of four [63,65]Cu hyperfine (hf) signals ([63,65]Cu, *I* = 3/2) coincide when the magnetic field is parallel to the crystallographic monoclinic *b*-axis or when the field is located in the *ac*-plane of the single-crystal. In some orientations of the crystal with respect to the external magnetic field, forbidden copper hf lines with $\Delta m \geqslant 1$ were

observed. Hyperfine interactions with ^{33}S nuclei of the donor atoms, which have been analyzed for similar copper complexes [21–23], could not be detected due to a low signal-to-noise ratio. A typical spectrum is shown in Fig. 3.

The principal values of the measured g and copper hf tensors are listed in Table II. For comparison, Table II also contains the corresponding values published for the systems $(Ph_4As)_2[Cu/Zn(mnt)_2]$ [15], $Cu/Zn(Et_2dtc)_2$ [14], $Bu_4N[Cu/Ni(mnt)(Et_2dtc)]$ [12] and $(MB)_2[Cu(mnt)_2]$ [24] (MB = methylene blue cation). Whereas the principal axes of g_1 and $A_1{}^{Cu}$ coincide, an angle of 15° was found between the principal axes of $\tilde{g}$ and $\tilde{A}^{Cu}$ in the plane of the smallest anisotropy, indicating a very low symmetry of the copper guest molecules.

In order to get more information about the actual structure of the $[Cu(mnt)(Et_2dtc)]^-$ anions in the host lattice, Extended Hückel MO calculations were performed. Considering the approximate tetrahedral structure of the zinc host complex, one would expect a rotation of one or both ligands of $[Cu(mnt)(Et_2dtc)]^-$ to a position in between the planar and tetrahedral arrangement, as observed for $[Cu/Zn(mnt)_2]^{2-}$ [15]. Therefore, the MOs, energies, g and A^{Cu} tensors were calculated for

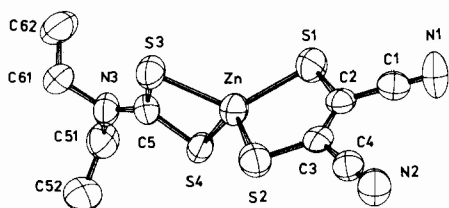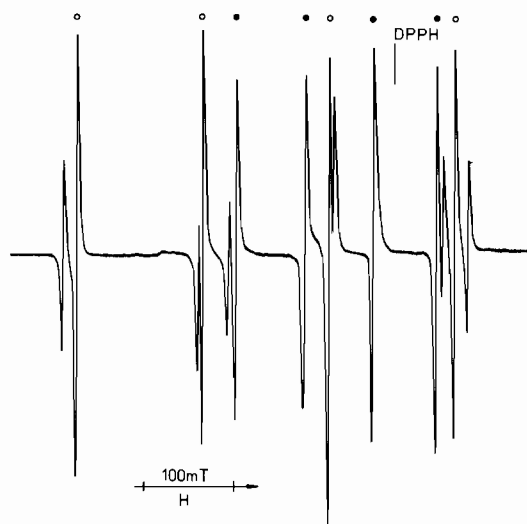Fig. 2. Structure and numbering of the anion.

Fig. 3. ESR spectrum of $Ph_4As[Cu/Zn(mnt)(Et_2dtc)]$(arbitrary direction of H_0 with respect to the crystal axes). The two different sites are marked by ○ and ●.

various angles between the ligand planes. The bond lengths and angles needed for the Extended Hückel calculations were taken from the structure of the host complex $[Zn(mnt)(Et_2dtc)]^-$. The values for the empirical parameters and the basis set are those used for the calculations on $Cu(Et_2dtc)_2$ [25, 26]. A Wolfsberg–Helmholz parameter of 2.5 was found to give the best results with respect to the EPR parameters. which were calculated with the formulas given in the cited papers.

The MO of the unpaired electron in the planar $[Cu(mnt)(Et_2dtc)]^-$ anion consists of the $3d_{xy}$ orbital of copper (coefficient $c_{3d_{xy}} = 0.715$) and hybrids of the 3s, $3p_x$ and $3p_y$ orbitals of sulfur donor atoms.

TABLE II. Comparison of the Spin-Hamiltonian Parameters of the Mixed Ligand System $Ph_4As[Cu/Zn(mnt)(Et_2dtc)]$[a] and Similar Systems Measured in Single-crystal Experiments

	$Ph_4As[Cu/Zn(mnt)-(Et_2dtc)]$	$(Ph_4As)_2-[Cu/Zn(mnt)_2]$ [15]	$Cu/Zn-(Et_2dtc)_2$ [14]	$Bu_4N[Cu/Ni(mnt)-(Et_2dtc)]$ [24]	$(MB)_2-[Cu(mnt)_2]$ [25]
g_1	2.090	2.089	2.108	2.084	2.090
g_2	2.028	2.024	2.031	2.024	2.024
g_3	2.020	2.017	2.023	2.020	2.024
g_{av}	2.046	2.043	2.054	2.043	2.046
A_1[b]	−140.3	−110.0	−142.4	−160.0	−142.4
A_2	−36.9	−20.3	−29.9	−42.4	−31.4
A_3	−27.6	−13.4	−20.4	−37.8	−31.4
A_{av}	−68.3	−47.9	−64.2	−80.4	−68.4

[a]Experimental errors: $g_i \pm 0.002; A_1{}^{Cu} \pm 0.5, A_{2,3}{}^{Cu} \pm 1.5$. [b]Hyperfine coupling parameters in 10^{-4} cm^{-1}.

The rotation of one ligand results in a mixing of the above mentioned atomic orbitals with the p_z orbitals of copper and sulfur. The main effect of this mixing is a reduction of the anisotropic hf couplings of copper, because the contributions of the p_z and d orbitals to the coupling constants counteract each other. Changes in the *g* tensor in going from the planar to the tetrahedral structure of [Cu(mnt)-(Et₂dtc)]⁻ are difficult to assess, since it must be expected that the largest effects on *g* will arise via changes in excited-state energies.
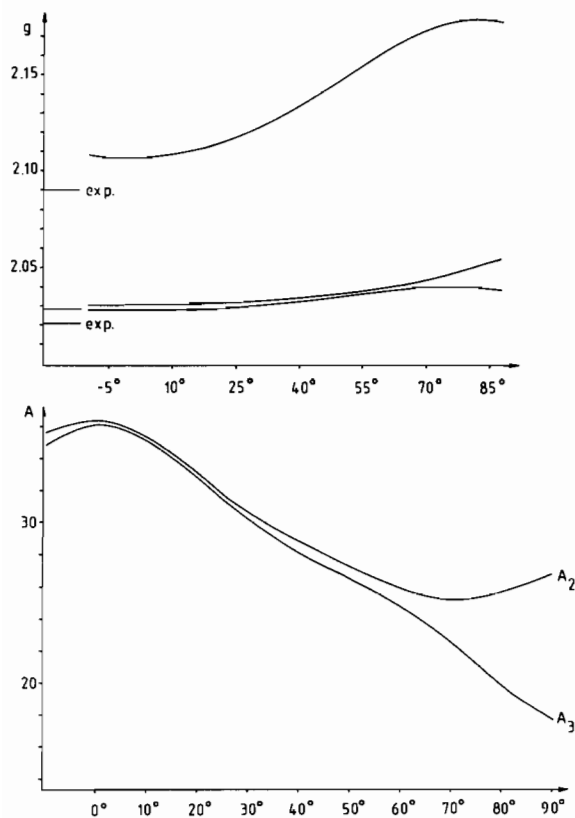
TABLE III. Comparison between Experimental and Calculated EPR-Parameters for [Cu/Zn(mnt)(Et₂dtc)]⁻. A in 10^{-4} cm⁻¹

	Experimental values	Calculated values	
		Planar structure	Dihedral angle 10°
g_1	2.090	2.106	2.108
g_2	2.028	2.030	2.031
g_3	2.020	2.028	2.028
g_{av}	2.046	2.055	2.056
A_1^{Cu}	−72.0	−72.4	−70.5
A_2^{Cu}	+31.3	+36.1	+35.1
A_3^{Cu}	+40.7	+36.3	+35.4
A_{av}^{Cu}	−68.3	−	−

Fig. 4. Variation of the principal values of *g* and A^{Cu} for various angles between the ligand planes. For A^{Cu} the graphs are made for the tracless part of the tensor. Only the two small tensor components are included. The third one is $-(A_2 + A_3)$. First and second order contributions as well as the influence of the copper 4p orbitals were taken into account.

Figure 4 shows the variation of the principal values of $\tilde{g}$ and $\tilde{A}_{Cu}$ for various angles between the ligand planes. It should be noted that the tensors are unreliable for angles close to 90°, because then the ground state is almost degenerate and use was made of non-degenerate perturbation theory for the calculation of $\tilde{g}$ and $\tilde{A}_{Cu}$. For the calculation of the hf tensor, first and second order contributions as well as copper 4p orbitals were taken into account.

The anisotropy in the *xy* plane is not reflected by the almost axial hf tensor calculated. With $(A_2 + A_3)/2 = A_\perp$, it can be seen from Fig. 4 that the dihedral angle between the ligand planes is not larger than 10°. The corresponding principal values (dihedral angles 0° and 10°) are listed in Table III.

This result is very surprising with respect to the tetrahedral structure of the host complex and the investigations reported for the system [Cu/Zn-(mnt)₂]²⁻ [15]. For [Cu(mnt)₂]²⁻ incorporated into [Zn(mnt)₂]²⁻ (dihedral angle 84°), an angle of 30° between the ligand planes was found.

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