4. Metal Complexes with Macrocyclic Ligands

Part XIX[1])

Synthesis and Cu^{2+}-Complexes of a Series of 12-, 14- and 16-Membered *cis*- and *trans*-N_2S_2-Macrocycles

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Summary

A series of 12-, 14-, and 16-membered N_2S_2-macrocyles (**9–11** and **19–21**) with *cis*- and *trans*-arrangement of the heteroatoms have been synthesized by high-dilution cyclization and subsequent reduction of the amides with B_2H_6. With these ligands the corresponding Cu^{2+}-complexes were prepared and their UV/VIS spectra, their electrochemistry and their EPR properties have been studied. Generally three absorption bands at 270–320 nm, 330–370 nm and 530–620 nm can be observed in aqueous solution and these have been assigned to the $N \rightarrow Cu^{2+}$ and $S \rightarrow Cu^{2+}$ charge-transfer bands and to the d-d* transition, respectively. The cyclic voltammetry in CH_3CN shows in all cases a reversible or quasi-reversible Cu^{2+}/Cu^{+}-transition at potentials of 10–480 mV against SHE. The values of $g_{\parallel}$ and $A_{\parallel}$ obtained from EPR spectra indicate that the geometry of the Cu^{2+}-complex of the 14-membered *cis*-N_2S_2-macrocycle is less distorted than that of the other complexes.

Introduction. – Polyoxa- [2], polyaza- [3] and polythia-macrocycles [4] have attracted the attention of the coordination chemist and have been studied in great detail. Whereas the crown ethers mainly bind alkali and earth-alkali ions, the polyaza- and polythia-ligands are more prone to complex transition metal ions. However, they clearly differ in their complexation properties, since the aza-ligands are more selective against hard ions whereas the thia-ligands preferentially bind soft ions. The binding properties of macrocycles can additionally be made more specific and selective by combining different donor atoms in one ring system. So N,O-macrocycles have received much attention. The interesting complexing properties and selectivity of the oxaaza mono- and bicycles in binding alkali and earth alkali ions have been reviewed by *Lehn* [5]. *Lindoy et al.* [6] also have prepared a large series of N_2O_2-ligands and have

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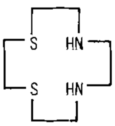
studied their metal complexes in detail. Much less is known about macrocycles with a N,S-donor set. The Ni^{2+}-complex of a *Schiff* base with a N_2S_2-donor set has been studied by *Busch et al.* [7]. This complex has also been reduced to give a 16-membered N_2S_2-macrocycle and the formation and dissociation kinetics with Cu^{2+} and Ni^{2+} were measured [8]. Furthermore the synthesis and metal complexes of N,S-macrocycles have been reported by *Tasker et al.* [9], *Hay et al.* [10] and *Lindoy et al.* [11], who prepared compounds with 14-, 15- and 16-membered rings. *Lehn et al.* [12] also described a 12-membered N_2S_2-macrocycle, the Cu^{2+}-complex of which has been studied electrochemically by *Gisselbrecht et al.* [13]. Finally *Rorabacher et al.* [4] have reported a NS_3- and two isomeric N_2S_2-macrocycles, which were included in their work on S_4-compounds for comparison purpose.

In the N_2S_2-ligands not only the ring size but also the arrangement of the donor atoms can be varied, since we have the possibility of a *cis*- and a *trans*-arrangement for the heteroatoms. To study systematically these effects we have prepared a series of *cis*- and *trans*-N_2S_2-ligands with ring size of 12, 14 and 16 atoms (**9–11** and **19–21**).



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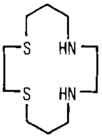

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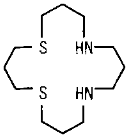

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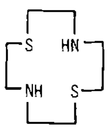

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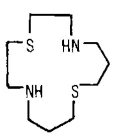

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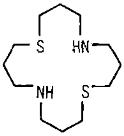

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Experimental. – Melting points (m.p.) obtained on a *Büchi* apparatus are uncorrected. IR spectra were run in KBr pills on a *Perkin Elmer 157G* spectrophotometer. ^{1}H-NMR spectra were obtained on a *Varian EM 360* instrument using TMS as internal standard. Elemental analysis were performed by the analytical laboratory of *Ciba-Geigy AG*, Basel.

The starting compounds were either purchased or prepared according to the literature and these latter were characterized by m.p., IR and NMR spectra: 2,2'-(ethylenedithio)diacetic acid **1** [14], 3,3'-(ethylenedithio)dipropionic acid **2** [14], bis(2-aminoethyl) sulfide **14** [15] and bis(3-aminopropyl) sulfide **15** [16].

3,3'-(Propylenedithio)dipropionic Acid (**3**). To 32 g (0.8 mol) NaOH and 42 g (0.4 mol) 3-mercaptopropionic acid in 400 ml H_2O/EtOH 4:1 29.4 g (0.26 mol) 1,3-dichloropropane were added and the mixture was refluxed for 5 h; EtOH was evaporated and the aq. solution acidified with conc. HCl to pH 2. The precipitate was filtered and washed with 0.1N HCl. The crystals were purified by recrystallization once from 0.1M HCl and once from 400 ml Et_2O. Yield 27.6 g (55%). M.p. 105–107°. ^{1}H-NMR ((D_6)DMSO): 1.7 (*quint.*, 2H, $C-CH_2-C$), 2.6 (*m*, 12H, 4 SCH_2, 2 CH_2COOH). $C_9H_{16}O_4S_2$ (252.34); found: C, 43.33; H, 6.21; S, 25.57%; calc.: C, 42.84; H, 6.39; S, 25.41%.

General Procedure for the Preparation of the Cyclic Amides. a) The acid chlorides were prepared by reacting 0.05–0.088 mol of the appropriate dicarboxylic acid with a 10-fold excess of $SOCl_2$ (*puriss.*) under stirring at 55°. After complete dissolution, the mixture was refluxed for 10 min. The excess of $SOCl_2$ was distilled off at 11 Torr and the residue treated three times with 50 ml toluene, which were distilled off to remove the last traces of $SOCl_2$. The residual oil of the acid chloride was used directly for the cyclization procedure.

b) The cyclization was performed using a high-dilution apparatus *(Normag AG)* under dry N_2 at – 5°–0°. 500 ml dry toluene were introduced into the reaction vessel; 0.05–0.088 mol of the acid chloride in 500 ml toluene and 0.1–0.176 mol diamine, also in 500 ml toluene were added simultaneously from two dropping funnels *(Normag AG)* at a rate of about 1 ml/min. After complete addition the mixture was filtered and the solid extracted several times with $CHCl_3$. The $CHCl_3$-phase was dried, filtered and evaporated, whereby the crude product resulted. In the case of **18** part of the product was dissolved in the toluene, so that this also had to be evaporated. For the analysis the products were recrystallized either from AcOH/Et_2O or HCOOH/Et_2O. *Table 1* gives a summary of the reactions, their yields, the solvent for recrystallization and the m.p. of the cyclic diamides.

Table 1. *Experimental Conditions for the High-Dilution Cyclization According to* Scheme 1 *and* 2

Diacid	Diamine	Product	Yield[a]) [%]	M.p.
1	**4**	**6**	37	250°
2	**4**	**7**	32	248–250°
3	**5**	**8**	44	209–210°
12	**14**	**16**	43	192–194° (195–196° [12])
13	**14**	**17**	38	203–205°
13	**15**	**18**	64	205–207°

[a]) After recrystallization from AcOH/Et_2O, except **6** from HCOOH/Et_2O.

3,6-Dithia-9,12-diazacyclododecane-1,8-dione (**6**). IR (KBr): 3280 (NH), 1650, 1520 (CONH). ^{1}H-NMR (CF_3COOH): 2.95 (*s*, 4H, 2 SCH_2; 3.5 (*s*, 4H, 2 SCH_2CO); 3.85 (*m*, 4H, 2 CH_2N); 8.0 (br., 2H, 2 NH). $C_8H_{14}N_2O_2S_2$ (234.33), found: C, 41.02; H, 6.01; N, 12.00; S, 27.21%; calc.: C, 41.01; H, 6.02; N, 11.95; S, 27.36%.

4,7-Dithia-11,14-diazacyclotetradecane-1,10-dione (**7**). IR (KBr): 3280 (NH), 1640, 1560 (CONH). ^{1}H-NMR (CF_3COOH): 3.0 (*m*, 12H, 4 SCH_2 and 2 CH_2CO); 3.83 (br., 4H, 2 CH_2N); 8.5 (br., 2H, 2 NH). $C_{10}H_{18}N_2O_2S_2$ (262.39); found: C, 45.67; H, 6.98; N, 10.47; S, 23.87%; calc.: C, 45.78; H, 6.92; N, 10.68; S, 24.44%.

4,8-Dithia-12,16-diazacyclohexadecane-1,11-dione (**8**). IR (KBr): 3260 (NH), 1620, 1550 (CONH). ^{1}H-NMR (CF_3COOH): 2.0 (*quint.*, 4H, 2 C–CH_2–C); 2.6-3 (*m*, 12H, 4 SCH_2 and 2 CH_2CO); 3.7 (br., 4H, 2 CH_2N); 8.3 (br., 2H, 2 NH). $C_{12}H_{22}N_2O_2S_2$ (290.44); found: C, 49.28; H, 7.47; N, 9.66; S, 21.87%; calc.: C, 49.63; H, 7.64; N, 9.65; S, 22.08%.

3,9-Dithia-6,12-diazacyclododecane-1,5-dione (**16**). IR (KBr): 3350 (NH), 1640, 1540 (CONH). ^{1}H-NMR (CF_3COOH): 2.9 (*t*, 4H, 2 SCH_2); 3.8 (*t*+*s*, 8H, 2 CH_2N, 2 CH_2CO); 8.3 (br., 2H, 2NH). $C_8H_{14}N_2O_2S_2$ (234.33); found: C, 40.80; H, 5.93; N, 11.75; S, 27.12%; calc.: C, 41.01; H, 6.03; N, 11.96; S, 27.37%.

4,11-Dithia-8,14-diazacyclotetradecane-1,7-dione (**17**). IR (KBr): 3400 (NH), 1650, 1560 (CONH). ^{1}H-NMR (CF_3COOH): 3.05 (*m*, 12H, 4 SCH_2, 2 CH_2CO); 3.75 (*m*, 4H, 2 CH_2N); 8.5 (br., 2H, 2 NH). $C_{10}H_{18}N_2O_2S_2$ (262.39); found: C, 45.70; H, 6.74; N, 10.61; S. 24.23%; calc.: C, 45.78; H, 6.92; N, 10.68; S, 24.44%.

4,12-Dithia-8,16-diazacyclohexadecane-1,7-dione (**18**). IR (KBr): 3300 (NH), 1635, 1565 (CONH). ^{1}H-NMR (CF_3COOH): 2.0 (*m*, 4H, 2 C–CH_2–C); 2.5–3.1 (*m*, 12H, 4 SCH_2 and 2 CH_2CO); 3.7 (*m*, 4H, 2 CH_2N); 8.4 (br., 2H, 2NH). $C_{12}H_{22}N_2O_2S_2$ (290.44); found: C, 49.36; H, 7.57; N, 9.46; S, 21.56%; calc.: C, 49.63; H, 7.64; N, 9.65; S, 22.08%.

General Procedure for the Reduction of the Cyclic Amides. Of analytical pure cyclic diamide (**6–8**, **16–18**) 4–8 mmol were dissolved in 10–50 ml abs. THF and purged with N_2. Then 16–32 mmol B_2H_6 (1M in THF, *EGA*) whose concentration was determined according to [17], were injected with a 20 ml syringe into the solution. The mixture was refluxed 2–6 h, whereby the reaction was followed by TLC (silica gel *Merck*, MeOH, R_f (diamide) $\approx$ 0.75, R_f (monoamide) $\approx$ 0.35, R_f (diamine) $\approx$ 0). After complete reaction the excess of B_2H_6 was destroyed by addition of a few ml MeOH, the clear solution was evaporated and the residue taken up with a mixture MeOH H_2O conc. HCl 20:5:2 and refluxed for 1 h. The solution was evaporated and the solid dissolved in 2.5M KOH. The aq. solution was then extracted three times with 10–20 ml CH_2Cl_2. The combined org. phases were dried (Na_2SO_4), filtered and evaporated. If the crude product was pure by TLC it was directly converted into the dihalide, otherwise it was chromatographed over a short *Alox* column with CH_2Cl_2 and 1–5% MeOH. The dihydrochlorides or dihydrobromides were obtained by dissolving the amine in MeOH or EtOH and adding an excess of 36% HCl or 47% HBr, respectively. The precipitates were recrystallized to give the analytically pure compounds. *Table 2* gives the experimental details and the melting points of the products.

1,4-Dithia-7,10-diazacyclododecane (**9**). ^{1}H-NMR ($CDCl_3$): 2.6 (*s*, 2H, 2NH); 2.5–3.0 (*m*+*s*, 16H, 4 CH_2N and 4 SCH_2). $C_8H_{20}Br_2N_2S_2$ (368.19); found: C, 25.85; H, 5.63; N, 7.72%; calc.: C, 26.10; H, 5.48; N, 7.61%.

1,4-Dithia-8,11-diazacyclotetradecane (**10**). ^{1}H-NMR ($CDCl_3$): 1.6 (*s*, 2H, 2 NH); 1.8 (*quint.*, 4H, 2 C-CH_2-C); 2.6–2.8 (2*t*, 8H, 2 S-CH_2-CH_2CH_2-N); 2.75 (*s*, 4H, SCH_2); 2.8 (*s*, 4H, NCH_2). $C_{10}H_{24}Cl_2N_2S_2$ (307.24); found: C, 39.22; H, 7.68; N, 9.17; S, 20.61%; calc.: C, 39.08; H, 7.87; N, 9.12; S, 20.86%.

Table 2. *Yields and M.p. of the N_2S_2-Macrocycle Dihalides Obtained by B_2H_6-Reduction of the Corresponding Diamides*

Diamide	Diamine·2HX	Reaction time [h]	Yield [%]	M.p.
6	**9**	7	46	192–4°
7	**10**	5	60	205–6°
8	**11**	7	34	195–6°
16	**19**	2	55	291–2°
17	**20**	5	64	281–2°
18	**21**	7	37	280–2°

1,5-Dithia-9,13-diazacyclohexadecane (**11**). ^{1}H-NMR ($CDCl_3$): 1.8 (2 *quint.*, 8H, 4 C-CH_2-C); 2.25 (*s*, 2H, 2NH); 2.5–2.9 (2*t*, 16H, 4 NCH_2 and 4 SCH_2). $C_{12}H_{28}Cl_2N_2S_2$ (335.40); found: C, 42.91; H, 8.23; N, 8.31%; calc.: C, 42.97; H, 8.42; N, 8.35%.

1,7-Dithia-4,10-diazacyclododecane (**19**). ^{1}H-NMR ($CDCl_3$): 2.5–3 (*m*, 16H, 4 CH_2N and 4 SCH_2); 3.3 (*s*, 2H, 2NH). $C_8H_{20}Br_2N_2S_2$ (368.19); found: C, 25.93; H, 5.28; N, 7.60%; calc.: C, 26.10; H, 5.48; N, 7.61%.

1,8-Dithia-4,12-diazacyclotetradecane (**20**). ^{1}H-NMR ($CDCl_3$): 1.9 (*m*, 4H, 2 C-CH_2-C); 2.0 (br., 2H, 2NH); 2.65–3.0 (*m*, 16H, 4 NCH_2 and 4 SCH_2). $C_{10}H_{24}Cl_2N_2S_2$ (307.34); found: C, 39.31; H, 7.83; N, 8.98%; calc.: C, 39.08; H, 7.87; N, 9.12%.

1,9-Dithia-5,13-diazacyclohexadecane (**21**). ^{1}H-NMR ($CDCl_3$): 1.66 (*s*, 2H, 2NH); 1.9 (*quint.*, 8H, 4 CCH_2C); 2.5–3.0 (*m*, 16H, 4 SCH_2 and 4 NCH_2). $C_{12}H_{28}Cl_2N_2S_2$ (335.40); found: C, 43.03; H, 8.18; N, 8.17%; calc.: C, 42.97; H, 8.42; N, 8.35%.

Preparation of the Cu^{2+}-Complexes. Ligand dihydrochloride or dihydrobromide (0.5 mmol) was dissolved in 2 ml 1M NaOH and this solution was extracted three times with 2 ml CH_2Cl_2. The free amine was obtained from the dried org. phase by evaporating the solvent. The free base was dissolved in 5 ml abs. MeOH and 0.5 mmol $Cu(ClO_4)_2 \cdot 6H_2O$ also in 5 ml abs. MeOH were added. The typical color of the Cu^{2+}-complex appeared and after some time the crystallization had begun. The solution was cooled to −18° and filtered. The crystals were washed with 1 ml cold abs. MeOH, then dried at 0.1 Torr. For the analysis the products were recrystallized once from abs. MeOH.

*Cu(**9**)(ClO_4)$_2$·H_2O.* Dark blue needles (73%). $C_8H_{18}Cl_2CuN_2O_8S_2 \cdot H_2O$ (486.83); found: C, 19.74; H, 4.11; N, 5.75%; calc.: C, 19.65; H, 4.12; N, 5.73%.

*Cu(**19**)(ClO_4)$_2$.* Turkish blue crystals (68%). $C_8H_{18}Cl_2CuN_2O_8S_2$ (468.81); found: C, 20.66; H, 4.19; N, 5.85%; calc.: C, 20.50; H, 3.87; N, 5.97%.

*Cu(**10**)(ClO_4)$_2$.* Violet crystals (60%). $C_{10}H_{22}Cl_2CuN_2O_8S_2$ (496.86); found: C, 24.29; H, 4.44; N, 5.75%; calc.: C, 24.17; H, 4.46; N, 5.64%.

*Cu(**20**)(ClO_4)$_2$.* Violet crystals (80%). $C_{10}H_{22}Cl_2CuN_2O_8S_2$ (496.86); found: C, 24.29; H, 4.66; N, 5.56%; calc.: C, 24.17; H, 4.46; N, 5.64%.

*Cu(**11**)(ClO_4)$_2$.* Violet needles (67%). $C_{12}H_{26}Cl_2CuN_2O_8S_2$ (524.92); found: C, 27.58; H, 5.13; N, 5.25%; calc.: C, 27.46; H, 4.99; N, 5.34%.

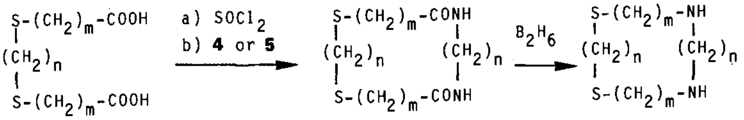
*Cu(**21**)(ClO_4)$_2$.* Blue violet crystals (46%). $C_{12}H_{26}Cl_2CuN_2O_8S_2$ (524.92); found: C, 27.46; H, 5.10; N, 5.18%; calc.: C, 27.46; H, 4.99; N, 5.34%.

Measurements. UV and VIS spectra in solution were run in 1-cm cells on a *Cary 118C*. The spectra of the solids were obtained by the nujol-technique [18]. The cyclic voltammograms were performed using a *Metrohm* VA-scanner *E612* and a VA-detector *E611* equiped with a *Hewlett Packard* plotter *7005B*. A three-electrode system was used: a *Beckman* Pt-disk electrode as working electrode, surrounded by a Pt-spiral as counter electrode and an Ag/AgCl reference electrode separated through a salt bridge. The experiments were carried out with $4 \cdot 10^{-4}$M Cu^{2+}-complex solutions in CH_3CN with 0.1M $LiClO_4$ at 25° ± 0.1°. To eliminate the effects of the diffusion potential $E_{1/2}$-values are referred to the $E_{1/2}$-value of the ferrocenium-ferrocene couple (+400 mV against SHE [19]) used as internal standard [20]. Cyclic voltammograms were recorded at scan rates of 5–30

mVs^{-1}. ESR spectra were obtained on a *Varian E9* spectrometer with a 9.5 GHz microwave bridge at −120° with 10^{-3}M complex solutions containing 30% EtOH. For calibration BDPA (α,γ-bisdiphenylene-β-phenylallyl radical, g = 2.00260) was used as external standard.

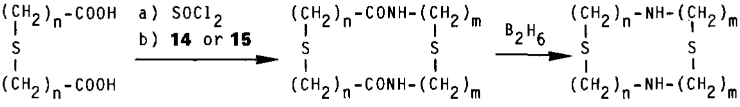
Results and Discussion. – The preparation of the six N_2S_2-macrocycles **9**–**11** and **19**–**21** follows the procedure which is based on the high-dilution cyclization of a diacid dichloride and a diamine to give a cyclic diamide [21]. In the case of the *cis*-N_2S_2-macrocycles the acids **1**–**3** were cyclized with 1,2-diaminoethane (**4**) and 1,3-diaminopropane (**5**) *(cf. Scheme 1)*. For the *trans*-N_2S_2-ligands, we have followed the procedure in [12] for the preparation of **19** and adapted it to the synthesis of **20** and **21** *(cf. Scheme 2)*.

Scheme 1



1 n=2, m=1	**6** n=2, m=1	**9** n=2, m=2
2 n=2, m=2	**7** n=2, m=2	**10** n=2, m=3
3 n=3, m=2	**8** n=3, m=2	**11** n=3, m=3

Scheme 2



12 n=1	**16** n=1, m=2	**19** n=2, m=2
13 n=2	**17** n=2, m=2	**20** n=3, m=2
	18 n=2, m=3	**21** n=3, m=3

The diamides were then reduced to the corresponding diamines with B_2H_6 in THF. All compounds of the *cis*- and *trans*-type were crystallized either as dihydrochlorides or dihydrobromides. The Cu^{2+}-complexes were prepared in straightforward manner by the reaction of the free ligand with an equimolar amount of $Cu(ClO_4)_2 \cdot 6H_2O$ in MeOH or EtOH. Their UV and VIS spectra in the solid state, in H_2O and in MeCN-solution were measured and are reported in *Table 3*.

The spectra of the complexes with the 12-membered N_2S_2-macrocycles **9** and **19** are relatively insensitive to the medium and the nature of the solvent, whereas those of the

Table 3. *Absorption Maxima* [nm] *and Molar Absorptivities* [$\mathrm{M}^{-1}\mathrm{cm}^{-1}$] *of the* Cu^{2+}*-Complexes with* **9**–**11** *and* **19**–**21**

Ring	Ligand	Solid b)	CH_3CN	H_2O
12	**9**	630 346	620 (803), 343 (4800)	620 (610), 356 (4600), 270 (2000)
	19	630 385	620 (727), 390 (4800)	620 (505), 375 (4800), 295 (1500)
14	**10**	506 346	527 (435), 336 (8900)	533 (386), 335 (9500), 267 (3100)
				533 (340), 337 (7700) [4]
	20	530 382	554 (465), 373 (9600)	565 (400), 370 (8900), 300 (2800)
16	**11**	530 353	584 (467), 370 (7200)	607 (500), 362 (5500), 280 (2000)
	21	540 365 320sh	a)	625 (550), 360 (5000), 320 (3200)

a) The solution is not stable.

b) Using the nujol technique [18].

Cu^{2+}-complexes with the 14-membered N_2S_2-macrocycles **10** and **20** exhibit a small shift to longer wavelengths on going from the solid to MeCN and H_2O. In the spectra of the Cu^{2+}-complexes with the 16-membered N_2S_2-ligands **11** and **21** the shift is much more pronounced. This seems to indicate that the metal ion is relatively well masked by the smaller rings, whereas it is accessible to the solvent in the case of the 16-membered macrocycles. Of course this could also be indicative for structural differences between the complex in the solid state and in solution.

The three bands observed in aqueous solution at 270–320 nm, 335–375 nm and 530–625 nm can be explained, by similarity to the CuN_2S_2-chromophore described in [15] [22], to the (N)→Cu^{2+} LMCT (ligand-to-metal charge transfer), the (S)→Cu^{2+} LMCT and to the ligand-field (LF) bands (d-d* transition), respectively. The energy difference between the (N)→Cu^{2+} LMCT and the (S)→Cu^{2+} LMCT range for our complexes from 6500 to 8100 cm^{-1} which is reasonable [22].

If the spectra of the Cu^{2+}-complexes of the 14-membered N_4- (512 nm) [23], *cis*-N_2S_2- (533 nm), *trans*-N_2S_2- (565 nm) and S_4-macrocycle (570 nm) [24] are compared, the trend is clear and the thioether S-atom fits into the spectrochemical series, having a somewhat weaker LF than the amine N-atom [25]. For the S_4-macrocycles, however, the 570-nm band was not assigned to a LF band but to a (S)→Cu^{2+} LMCT, since the Cu-S stretching mode at 274 cm^{-1} did not show a resonance enhancement with the 570-nm band [26]. Interesting is the gradual increase of the molar absorptivity for this band: for the Cu^{2+}-complex with the N_4-macrocycle 100$\mathrm{M}^{-1}\mathrm{cm}^{-1}$, for that with the *cis*-N_2S_2-ligand 386$\mathrm{M}^{-1}\mathrm{cm}^{-1}$ and for that with the S_4-ligand 1900$\mathrm{M}^{-1}\mathrm{cm}^{-1}$. This might indicate that the pure LF-band (d-d*-transition) of the Cu^{2+}-complex with the N_4-ligand gains intensity by mixing with CT contributions when N-donors are replaced by S-atoms. The position of the so-called LF-band in our complexes which range from 530 to 625 nm depending on the ring size and the *cis*- and *trans*-position of the donor atoms probably reflects structural changes along this series of complexes. The $E_{1/2}$-values of the Cu^{2+}/Cu^{+}-couple determined by cyclic voltammetry (CV) are listed in *Table 4* and one of the experiments is shown in *Fig. 1*. For the Cu^{2+}-complexes of the 12-membered *cis*- and *trans*-ligands **9** and **10** the CV is nearly reversible as indicated by a peak separation ΔE of 84–88 mV under conditions in which the internal standard ferrocenium/ferrocene gives $\Delta E = 64$ mV. Also the other criteria for reversibility are fulfilled:

Table 4. *Results from CV of the Cu^{2+}-Complexes with the N_2S_2-Ligands* **9–11** *and* **19–21** *and the Parent Compounds with N_4- and S_4-Donor Set*

Ring	N_4-Donor c)	N_2S_2-Donor d)		S_4-Donor c)	
	$E_{1/2}$ a)	$E_{1/2}$ a)	ΔE b)	$E_{1/2}$ a)	ΔE b)
12 *cis*	− 397[25]	164	84	641 [4]	72
trans		132 (140c)[13])	88 (70c))		
14 *cis*	− 474[25]	12 (76c)[4])	120 (181c))	600 [4]	63
trans		172	148		
16 *cis*		368	160	771 [4]	70
trans		484	146		

a) All values in mV against SHE.
b) Potential difference between the cathodic and anodic peak in mV.
c) In H_2O.
d) In CH_3CN with 0.1M $LiClO_4$.

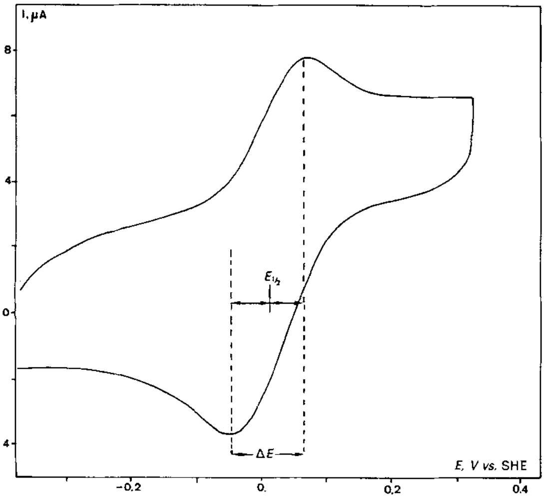


Fig. 1
Cyclic voltammogram of the Cu^{2+}-complex ($4 \cdot 10^{-4}$M) with **10** *in CH_3CN at 10 mVs^{-1}*. The parameters $E_{1/2}$ and ΔE are defined in the text.

so $i_a/i_c = 1$ and the peak separation stays constant for scan rates between 5 and 30 mVs^{-1}. On the other hand the Cu^{2+}-complexes of both 14- and 16-membered macrocycles (**10**, **11**, **20**, **21**) are quasi-reversible. The peak separation is over 120 mV, although i_a/i_c is still about 1. Hence it appears that in the case of the 12-membered ligands **9** and **10** little or no rearrangement of the structure of the complex takes place when Cu^{2+} is reduced to Cu^{+}. This might be due to the non-planarity of these Cu^{2+}-complexes, since the 12-membered rings cannot encircle the metal ion. For the larger rings, however, the Cu^{2+}-ion fits into the ring so that the typical square planar geometry for Cu^{2+} can be achieved. Since this is not ideal for Cu^{+}, a structural rearrangement is necessary after electron transfer. The $E_{1/2}$-values of the complexes with the 16-membered rings **11** and **21** are the highest ones, followed by those of the Cu^{2+}-complexes with **20**, **9** and **19**, whereas the Cu^{2+}-complex with the 14-membered *cis*-ligand **10** has the lowest value. The 16-membered macrocycles, being more flexible, can adapt themselves to preferentially bind Cu^{+} over Cu^{2+}. Comparing the $E_{1/2}$-value for the macro-

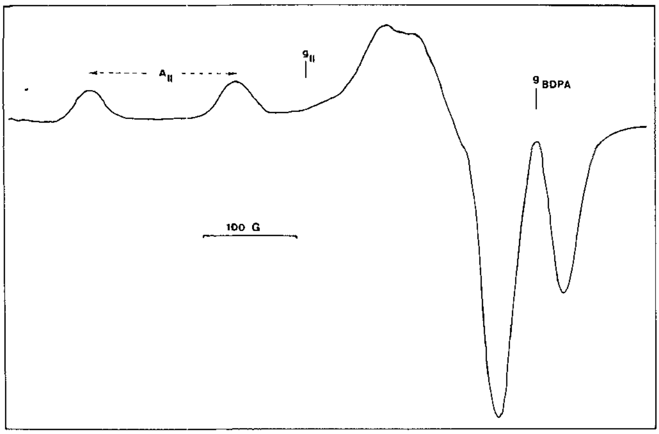


Fig. 2
ESR spectrum of the Cu^{2+}*-complex with* **19** *in 30%* $EtOH/H_2O$ *at −120°.* The value of the standard BDPA, $g_{\|}$ and $A_{\|}$ are indicated.

Table 5. *ESR Results for the* Cu^{2+}*-Complexes with* **9–11** *and* **19–21** *and the Parent Compounds with* N_4*- and* S_4*-Donor Set*

Ligand	$g_{\|}$	$A_{\|} \cdot 10^4\ cm^{-1}$	Ligand	$g_{\|}$	$A_{\|} \cdot 10^4 cm^{-1}$
9	2.174	152	**20**	2.162	161
10	2.145	170	**21**	[a])	[a])
11	2.172	151	[14]aneN_4 [b])	2.186	205
19	2.171	145	[14]aneS_4 [c])	2.10	165

[a]) The spectrum is an overlap of two species.
[b]) From [28].
[c]) From [4].

cycles with a N_4-, N_2S_2- and S_4-donor set the sequence for $E_{½}$ is $E_{½}(N_4) < E_{½}(N_2S_2) < E_{½}(S_4)$ for each ring size (see *Table 4*). This is in accordance with the observation of other authors [4] [27].

The EPR spectra of the Cu^{2+}-complexes were measured in a glass at −120°. One example is shown in *Fig. 2*. No attempt was made to fit the spectra to obtain all the parameters. Instead, only the $A_{\|}$- and $g_{\|}$-values were determined graphically. These values *(Table 5)* are typical for N_2S_2-ligands [29] and show a rough correlation between $g_{\|}$ and $A_{\|}$ as previously noted by other authors [29] [30]. From the low $g_{\|}$- (2.145) and high $A_{\|}$- (170.10^{-4} cm^{-1}) values for the Cu^{2+}-complex with **10** we would expect the smallest distortion from square planar geometry for this complex along the series of our Cu^{2+}-N_2S_2-complexes. This is also in accordance with the strongest LF found for the Cu^{2+}-complex of **10** in comparison with the other ones (see *Table 3*). The 12-membered macrocycles **9** and **19**, being to small, and the 16-membered macrocycle **11**, being to large and to flexible, probably form distorted complexes. The 14-membered *trans*-N_2S_2-macrocycle **20**, having the sequence [2,2,3,3], gives a less strong LF as the *cis*-N_2S_2-ligand **10**. This also has been observed in the case of the corresponding 14-membered N_4-macrocycle [31].

In conclusion one can say that the Cu^{2+}-complexes with the N_2S_2-macrocycles **9–11** and **19–21** show properties, such as UV/VIS spectra, electrochemical behavior and EPR data which are in between those of the complexes with N_4- and S_4-macrocycles. However, the ring size and the relative position of the hetero atoms also have their specific effects. Interesting is that the Cu^{2+}-complex with the 14-membered ligand **10** seems to be the one which has the strongest LF and the less distorted structure. Hence, as in the case of the N_4-macrocycles the ring size of fourteen with a bridging sequence of [2, 3, 2, 3] seems ideal to encircle a metal ion such as Cu^{2+}.

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