recorded on a Stoe-Siemens-Huber four-circle diffractometer equipped with a Siemens SMART CCD area detector. The reflections were collected at $-140\,^\circ C$ on a shock-cooled crystal of dimensions $0.4 \times 0.3 \times 0.2\ mm^3$ in a drop of oil[20] with a $2\theta/\omega$-scan in the range $5.0 \leq 2\theta \leq 49.6^\circ$. Of the 21552 observed reflections, 3333 were independant ($R_{int} = 0.033$). The structure was solved by direct methods (SHELXS-97)[21] and refined against F^2.[22] The hydrogen atoms were placed in ideal positions and refined with a riding model that allows the rotation of the methyl groups about their local axes; max./min. residual electron density after the final difference Fourier synthesis $207/-174\ e\,nm^{-3}$, $R1 = 0.027$ ($I > 2\sigma(I)$) and $wR2 = 0.060$ (all data). The values of $R1$ and $wR2$ are defined as $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR2 = \{[\Sigma w(F_o^2 - F_c^2)^2]/[\Sigma w(F_o^2)^2]\}^{1/2}$. The absolute structure was determined by refinement of the Flack parameter[23] to 0.0(1). A total of 181 parameters were refined.[15b]

[11] C. Böker, Dissertation, Universität Göttingen, **1995**.

[12] a) A. Haaland, O. Stokkeland, *J. Organomet. Chem.* **1975**, *94*, 345; b) R. Benn, E. Janssen, H. Lehmkuhl, A. Rufinska, K. Angermund, P. Betz, R. Goddard, C. Krüger, *ibid.* **1991**, *411*, 37; c) B. Cetinkaya, P. B. Hitchcock, H. A. Jasim, M. F. Lappert, H. D. Williams, *Polyhedron* **1990**, *9*, 239.

[13] R. T. Sanderson, *Polar Covalence*, Academic Press, New York, **1983**, 147.

[14] The ^{27}Al NMR spectrum of **2** did not contain any signals.

[15] a) Crystal structure analysis of $\mathbf{2}\cdot C_6H_{14}O$: $C_{46}H_{122}Al_4OSi_{12}$, $M_r = 1136.44$, orthorhombic, space group $P2_12_12_1$, $a = 1367.8(1)$, $b = 1763.7(2)$, $c = 2966.8(3)$ pm, $V = 7.157(1)\ nm^3$; $Z = 4$, $\rho_{calcd} = 1.055\ g\,cm^{-3}$, $F(000) = 2504$, $\lambda = 71.073$ pm, $\mu(Mo_{K\alpha}) = 0.295\ mm^{-1}$. The data were collected on a Stoe-Siemens four-circle diffractometer. The reflections were measured at $-130\,^\circ C$ on a shock-cooled crystal of dimensions $1.0 \times 0.5 \times 0.4\ mm^3$ in a drop of oil[20] by a $2\theta/\omega$-scan in the range $7.0 \leq 2\theta \leq 50.1^\circ$. Of the 7476 observed reflections, 7290 were independent; max./min. residual electron density after the final difference Fourier synthesis $413/-330\ e\,nm^{-3}$, $R1 = 0.046$ ($I > 2\sigma(I)$) and $wR2 = 0.117$ (all data). The structure was solved by direct methods (SHELXS-97)[21] and refined against F^2 (SHELXL-97).[22] The structure was refined as a racemic twin. b) Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-101096. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44) 1223336-033; e-mail: deposit@ccdc.cam.ac.uk).

[16] R. C. Weast, *Handbook of Chemistry and Physics*, 54th ed., CRC-Press, Cleveland, **1973**.

[17] a) W. Uhl, J. Wagner, *Angew. Chem.* **1991**, *103*, 182; *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 179; b) W. Uhl, *Z. Naturforsch. Sect. B* **1988**, *43*, 1113.

[18] G. Linti, *J. Organomet. Chem.* **1996**, *520*, 107.

[19] C. Schnitter, H. W. Roesky, T. Albers, H.-G. Schmidt, C. Röpken, E. Parisini, G. M. Sheldrick, *Chem. Eur. J.* **1997**, *3*, 1783.

[20] T. Kottke, D. Stalke, *J. Appl. Crystallogr.* **1993**, *26*, 615.

[21] G. M. Sheldrick, *Acta Crystallogr. Sect. A* **1990**, *46*, 467.

[22] G. M. Sheldrick, SHELXL, A Program for Crystal Structure Refinement, Universität Göttingen, **1997**.

[23] H. D. Flack, *Acta Crystallogr. Sect. A* **1983**, *39*, 876.

$TeS_2^{\bullet-}$ Radical Anions in $CuBrCu_{1.2}TeS_2$**

Arno Pfitzner,* Frank Baumann, and Wolfgang Kaim*

Dedicated to Professor W. H. E. Schwarz
on the occasion of his 60th birthday

Copper(I) halides have recently proven to be "solid solvents" for molecules of the elements of Groups 15 and 16. Thus, neutral and low-charged phosphorus polymers were detected and structurally characterized in, for example, $(CuI)_3P_{12}$[1] and $(CuBr)_{10}Cu_2P_{20}$.[2] Compounds of copper(I) halides with selenium or tellurium contain neutral homoatomic chains, such as $^1_\infty[Te]$ in $CuClTe_2$,[3] or six-membered rings, as in $CuISe_3$.[4] Heteroatomic chalcogen chains in which selenium and tellurium ($^1_\infty[SeTe]$[5]) or sulfur and tellurium atoms alternate ($^1_\infty[STe]$[6]) can also be obtained in a copper(I) halide matrix. In $CuISe_{1.93}Te_{1.07}$ tellurium-rich six-membered rings $Se_{6-x}Te_x$ ($x \leq 3$) were detected for the first time in the solid state.[7] Degradation of the neutral chalcogen chains $^1_\infty[STe]$ led to $(CuI)_3Cu_2TeS_3$, which is the first copper chalcogenide halide to contain a complex thiotellurate(IV) ion.[8] Like $(CuI)_2Cu_3SbS_3$,[9] this compound can be described as a composite compound of copper(I) iodide and a copper thiometalate.

Here we report the preparation, crystal structure determination, and ESR spectroscopic investigations of $CuBrCu_{1.2}TeS_2$ (**1**). In this compound the novel $TeS_2^{\bullet-}$ radical anion and the unknown polychalcogenide ion TeS_2^{2-} were identified and structurally characterized. Compound **1** crystallizes as very thin, square or rectangular black platelets. Top illumination of the crystals indicates their tendency for twinning by a characteristic reflection pattern. Scanning electron micrographs of the edge of a broken platelet (Figure 1) show the pronounced two-dimensional character of the solid compound. The thickness of the single sheets is significantly smaller than 1 µm. Nevertheless, the crystal structure could be determined.[10] Figure 2a shows the three-dimensional structure of **1**. The copper atoms Cu4, which are located between the layers on a position with an occupancy of 20%, are omitted in order to emphasize the two-dimensional character of the structure. The layers are stacked along [001] and are made up of tetrahedrally coordinated copper atoms. The coordination polyhedra are $[CuBr_2S_2]$ for Cu1 and Cu2, and $[CuS_4]$ for Cu3. The Cu–S distances are 2.288 Å, and the Cu–Br distances 2.512 Å. The $[CuS_4]$ polyhedra are located in the center, and the $[CuBr_2S_2]$ polyhedra at the upper and lower borders of the layers. Further building blocks are bent TeS_2

---

[*] Dr. A. Pfitzner
Institut für Anorganische Chemie der Universität-Gesamthochschule
D-57068 Siegen (Germany)
Fax: (+49) 271-740-2555
E-mail: pfitzner@chemie.uni-siegen.de

Prof. Dr. W. Kaim, Dipl.-Chem. F. Baumann
Institut für Anorganische Chemie der Universität
Pfaffenwaldring 55, D-70550 Stuttgart (Germany)
Fax: (+49) 711-685-4165
E-mail: kaim@iac.uni-stuttgart.de

[**] The support of Professor Deiseroth and the financial assistance from the Deutsche Forschungsgemeinschaft is gratefully acknowledged.

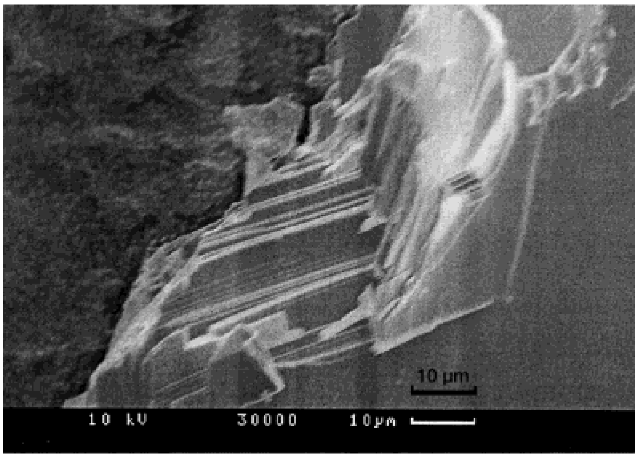

Figure 1. Scanning electron micrograph (× 1200) of the edge of a broken platelet of **1**. The thickness of the layers is significantly smaller than 1 µm.

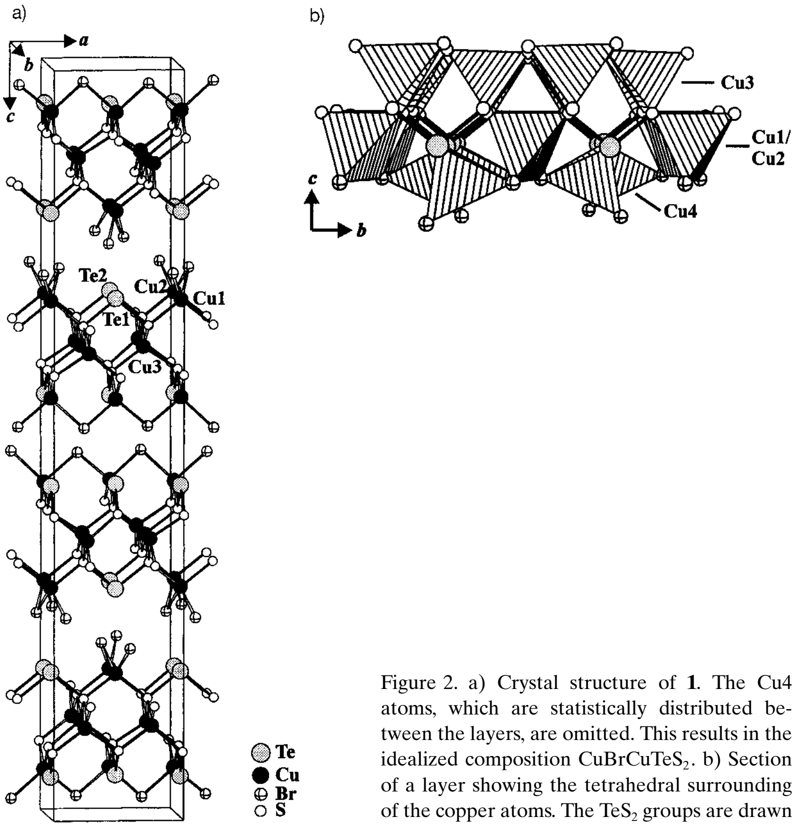

Figure 2. a) Crystal structure of **1**. The Cu4 atoms, which are statistically distributed between the layers, are omitted. This results in the idealized composition $\mathrm{CuBrCuTeS_2}$. b) Section of a layer showing the tetrahedral surrounding of the copper atoms. The $\mathrm{TeS_2}$ groups are drawn in bold.

groups. Assuming a composition of $\mathrm{CuBrCuTeS_2}$ (see Figure 2a) these groups bear a total charge of -1; that is, they are radical anions $\mathrm{TeS_2^{\bullet -}}$.

However, the corresponding stoichiometric compound $\mathrm{CuBrCuTeS_2}$ has not yet been obtained. The structure of **1** can be formally derived from this hypothetical compound by intercalating 0.2 copper atoms per formula unit between the layers. The resulting compound can be described as $\mathrm{(CuBr)_5Cu_6[TeS_2]_4{}^{\bullet -}[TeS_2]^{2-}}$. Despite the mixed-valent character, copper occurs exclusively as tetrahedrally coordinated $\mathrm{Cu^+}$ ions. The $\mathrm{TeS_2^{\bullet -}}$ and $\mathrm{TeS_2^{2-}}$ units cannot be distinguished by X-ray diffraction data at room temperature. Two almost identical $\mathrm{TeS_2}$ groups with Te–S distances of 2.375 Å are present in the crystal structure. The Te–S bond length is similar to those in the $\mathrm{TeS_3^{2-}}$ ions of $\mathrm{(CuI)_3Cu_2TeS_3}$,[8] $\mathrm{ACuTeS_3}$, and $\mathrm{AAgTeS_3}$ (A = alkali metal[12]), but is about 0.11 Å shorter than that in the formally neutral chalcogen chains (${}^{1}_{\infty}$[STe]) of CuXSTe (X = Cl, Br).[6] This unexpected finding can be explained by the number of covalent S–Te bonds, that is, one per sulfur atom in $\mathrm{TeS_2}$ and in $\mathrm{TeS_3^{2-}}$, but two in ${}^{1}_{\infty}$[STe]. The average S-Te-S bond angle of 101.9° in $\mathrm{TeS_2^{\bullet -}}$ is slightly larger than that of ${}^{1}_{\infty}$[STe] and about 3–5° larger than that of $\mathrm{TeS_3^{2-}}$ in $\mathrm{(CuI)_3Cu_2TeS_3}$. In contrast to the heteroatomic polychalcogenide ions $\mathrm{[S_xSe_{4-x}]^{2-}}$ in α-$\mathrm{CsCu(S_xSe_{4-x})}$ and $\mathrm{[S_xSe_{6-x}]^{2-}}$ in $\mathrm{CsCu(S_xSe_{6-x})}$,[13] the positions of the different chalcogen atoms in the $\mathrm{TeS_2}$ groups can be clearly distinguished. Tellurium occupies exclusively the central position, whereas sulfur is located only at the terminal positions.

The crystal structure arrangement is responsible for the pronounced layer character of **1**. The $\mathrm{[CuS_4]}$ groups are located in the center and the $\mathrm{[CuS_2Br_2]}$ polyhedra at the borders of the layers. However, it is not possible to extend the layers to form a regular three-dimensional tetrahedral structure. Both sulfur and tellurium are coordinated to copper (Figure 2b), but tellurium occupies "cation sites" in the structure. As a consequence, the construction of a three-dimensional tetrahedral structure is terminated at the tellurium positions (Figure 2b).

The novel anion $\mathrm{TeS_2^{\bullet -}}$ is a further member of the large group of triatomic radicals with 19 valence electrons and a ${}^2\mathrm{B}_1$ ground state.[14] Other relatively stable compounds that predominantly consist of light atoms are the radicals $\mathrm{ClO_2^{\bullet}}$[15] and $\mathrm{SO_2^{\bullet -}}$[16] (which is in equilibrium with $\mathrm{S_2O_4^{2-}}$) as well as the homologous radicals $\mathrm{SeO_2^{\bullet -}}$,[17] $\mathrm{NO_2^{\bullet 2-}}$,[18] $\mathrm{NF_2^{\bullet}}$,[19] the ozonide ion $\mathrm{O_3^{\bullet -}}$,[20] and the deep blue $\mathrm{S_3^{\bullet -}}$ ion[21] (a component of lapis lazuli[22]). A survey of ESR investigations of this class of radicals, including a discussion of correlations and an estimation of the participation of d orbitals, has been already published.[14]

A powder sample of **1** was investigated at 3.5 K in an X-band ESR spectrometer. An intense signal was observed with axial splitting of the *g* components within the limits of the linewidth (Figure 3, Table 1). Hyperfine splitting could not be detected.[23] Owing to very fast relaxation, the ESR signal broadens at higher temperature and is no longer visible. A similar observation was made for the main group radical $\mathrm{B_6I_6^{\bullet -}}$,[24] which is similar to $\mathrm{TeS_2^{\bullet -}}$ in that a 5p element with numerous available atomic states participates in the spin distribution.

$\mathrm{SeO_2^{\bullet -}}$, a lighter homologue of $\mathrm{TeS_2^{\bullet -}}$, also shows an almost axial splitting of the *g* components with $g_1 \gg g_2$, g_3; a similar pattern was observed for $\mathrm{O_3^{\bullet -}}$ (Table 1). As expected, the deviation of g_1 from the free electron value of 2.0023 and the *g* anisotropy $\Delta g = g_1 - g_3$ increase when light atoms are sub-

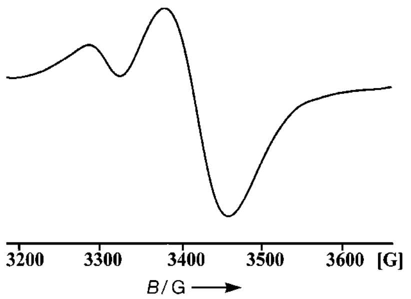

Figure 3. ESR spectrum of $\mathrm{CuBrCu_{1.2}TeS_2}$ at 3.5 K and 9.64281 GHz.

Table 1. ESR data of radicals with 19 valence electrons.

	g_1	g_2/g_3	$(g_\perp)$	$\Delta g = g_1 - g_3$	T [K]	Ref.
$\mathrm{O}_3^{\cdot-}$	2.0174	2.0025/2.0013	(2.0019)	0.0161	77	[20]
$\mathrm{SeO}_2^{\cdot-}$	2.0317	2.0066/1.9975	(2.0021)	0.0342	77	[17]
$\mathrm{TeS}_2^{\cdot-}$	2.0804	2.0085/2.0085[a]	(2.0085)	0.0719	3.5	this work

[a] g_2 and g_3 can differ by at most 0.01.

stituted by heavier homologues with much higher spin–orbit coupling constants (Table 1).[14, 17] Since a major part of the spin density of, for example, $\mathrm{SeO}_2^{\cdot-}$ is located at the central atom, g_1 and Δg are significantly higher when tellurium is present instead of selenium. The results of the ESR investigations (Figure 3), including the considerable linewidth and the fast relaxation, are in accord with the structural identification of $\mathrm{TeS}_2^{\cdot-}$. Thus, a new example has been added to this group of well-known inorganic radicals.

Experimental Section

$\mathrm{CuBrCu_{1.2}TeS_2}$ (**1**) was prepared by the reaction of stoichiometric amounts of CuBr, Cu, Te, and S in the ratio 1:1.2:1:2 in evacuated silica ampoules. The mixture of starting materials was melted at 600 °C, homogenized by grinding, and then tempered at 390 °C. Black, shiny square or rectangular platelets were obtained together with a microcrystalline powder after 14 d. The purity and the sample quality was checked by X-ray powder diffraction. Microcrystalline samples with the composition $\mathrm{CuBrCu_{1.2}TeS_2}$ were investigated at 3.5 K with an Bruker ESP300 X-band ESR spectrometer. The composition of selected single crystals was determined by semiquantitative energy dispersive X-ray analysis analysis (EDX): found: Cu:Br:Te:S = 0.350:0.169:0.158:0.324 (calcd: 0.355:0.161:0.161:0.322).

Received: February 5, 1998 [Z 11438 IE]
German version: *Angew. Chem.* **1998**, *110*, 2057–2059

Keywords: chalcogens · copper · EPR spectroscopy · radical ions · solid-state chemistry

---

[1] A. Pfitzner, E. Freudenthaler, *Angew. Chem.* **1995**, *107*, 1784; *Angew. Chem. Int. Ed. Eng.* **1995**, *34*, 1647.
[2] E. Freudenthaler, A. Pfitzner, *Z. Kristallogr.* **1997**, *212*, 103, and references therein.
[3] J. Fenner, *Acta Crystallogr. B* **1976,** *32*, 3084.
[4] W. Milius, A. Rabenau, *Mater. Res. Bull.* **1987**, *22*, 1493.
[5] A. Pfitzner, S. Zimmerer, *Z. Anorg. Allg. Chem.* **1995,** *621*, 969.
[6] A. Pfitzner, S. Zimmerer, *Z. Anorg. Allg. Chem.* **1996**, *622,* 853.
[7] A. Pfitzner, S. Zimmerer, *Z. Kristallogr.* **1997**, *212*, 203.
[8] A. Pfitzner, S. Zimmerer, *Angew. Chem.* **1997**, *109*, 1031; *Angew. Chem. Int. Ed. Eng.* **1997**, *36*, 982.
[9] A. Pfitzner, *Chem. Eur. J.* **1997**, *3*, 2032.
[10] X-ray structure determination of $\mathrm{CuBrCu_{1.2}TeS_2}$: tetragonal, space group $I4_1/a$ (no. 88), $a = 7.297(3)$, $c = 41.882(8)$ Å, $V = 2230.1(8)$ Å^3, $Z = 16$, $\rho_{\mathrm{calcd}} = 4.904$ g cm^{-3}. Data collection: 2139 reflections, 998 symmetry-independent reflections ($R_{\mathrm{int}} = 0.098$), room temperature, ω scans, $\mathrm{Mo_{K\alpha}}$ radiation, $\lambda = 0.71073$ Å, $2\theta_{\max} = 50°$, crystal dimensions $0.3 \times 0.3 \times 0.01$ mm, numerical absorption correction. Structure solution: direct methods, refinement against F^2 (full matrix, JANA98[11]), 64 refined parameters, R ($I > 3\sigma_{\mathrm{I}}$) = 0.0853, wR ($I > 3\sigma_{\mathrm{I}}$) = 0.1134, R (all reflections) = 0.1319, wR (all reflections) = 0.1166, GOF = 2.12, $\Delta\rho_{\min}/\Delta\rho_{\max} = -4.97/3.42$ e Å^{-3}. Twinning (4/*mmm*) was refined and gave a volume of 8% for the second individual. From the X-ray data neither a superstructure ordering of the $\mathrm{TeS}_2^{\cdot-}$ and the TeS_2^{2-} units (both tellurium atoms on 8*e*) nor ordering of the copper atoms Cu4 could be derived. Further details of the crystal structure investigations may be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, Germany (fax: (+49) 7247-808-666; e-mail: crysdata@fiz-karlsruhe.de), on quoting the depository number CSD-408253.
[11] V. Petricek, JANA98, Institute of Physics, Academy of Sciences of the Czech Republic, Prague, Czech Republic, **1997**.
[12] X. Zhang, M. G. Kanatzidis, *J. Am. Chem. Soc.* **1994**, *116*, 1890.
[13] C. R. Raymond, P. K. Dorhout, *Inorg. Chem.* **1996**, *35*, 5634.
[14] P. W. Atkins, M. C. R. Symons, *The Structure of Inorganic Radicals*, Elsevier, Amsterdam, **1967**.
[15] P. W. Atkins, J. A. Brivati, N. Keen, M. C. R. Symons, P. A. Trevalion, *J. Chem. Soc.* **1962**, 4785.
[16] W. G. Hodgson, A. Neaves, C. A. Parker, *Nature* **1956**, *178*, 489.
[17] P. W. Atkins, M. C. R. Symons, H. W. Wardale, *J. Chem. Soc.* **1964**, 5215.
[18] P. W. Atkins, M. C. R. Symons, *J. Chem. Soc.* **1962**, 4794.
[19] R. Ettinger, C. B. Colburn, *Inorg. Chem.* **1963**, *2*, 1311.
[20] P. W. Atkins, A. Horsfield, M. C. R. Symons, *J. Chem. Soc.* **1964**, 5220.
[21] J. H. Lunsford, D. P. Johnson, *J. Chem. Phys.* **1973**, *58*, 2079.
[22] F. Seel, G. Schäfer, H. J. Güttler, G. Simon, *Chem. Unserer Zeit* **1974**, *8*, 65.
[23] Much larger *g* factor components and ^{63}Cu/^{65}Cu hyperfine splitting are expected for Cu^{2+} in an approximately tetrahedral environment: S. Knapp, T. P. Keenan, X. Zhang, R. Fikar, J. A. Potenza, H. J. Schugar, *J. Am. Chem. Soc.* **1990**, *112*, 3452.
[24] V. Lorenzen, W. Preetz, F. Baumann, W. Kaim, *Inorg. Chem.*, in press.

Rapid Phosphodiester Hydrolysis by Zirconium(IV)

Reina Ott and Roland Krämer*

Nonenzymatic hydrolysis of the phosphodiester backbone of nucleic acids is an attractive research aim in molecular biology. Bioconjugates of hydrolytically active metal complexes and antisense-oligonucleotides may have important applications as artificial restriction enzymes since they have much greater sequence-specificitiy than their natural counterparts.[1] In addition, the treatment of incurable diseases by the in-vivo silencing of the genetic code of pathogenic proteins on the RNA or DNA level has been attempted.[2] RNA is more susceptible to hydrolysis than DNA and various low molec-

---

[*] Priv.-Doz. Dr. R. Krämer, R. Ott
Anorganisch-Chemisches Institut der Universität
Wilhelm-Klemm-Strasse 8, D-48149 Münster (Germany)
Fax: (+49) 251-833-8366
E-mail: kramerr@nwz.uni-muenster.de

1433-7851/98/3713-1957 $ 17.50+.50/0