

A Journal of

Zeitschrift für Naturforschung B

Chemical Sciences

Gegründet 1946 in den Instituten
der Max-Planck-Gesellschaft

Band 44 1989



Verlag der Zeitschrift für Naturforschung

Tübingen

Contents

<p>Contents of Number 1</p> <p><i>Original Communications</i></p> <p>Synthesis and Structure of Tetrameric N,N'-Diphenylformamidinato Gold(I), [Au(PhNCHNPh)]₄ (In German) E. HARTMANN and J. STRÄHLE 1</p> <p>Synthesis and Crystal and Molecular Structure of <i>trans</i>-Dichloro(ethanedial dioximate(1-)-N,N')-(ethanedial dioxime-N,N')rhodium(III) M. MÉGNAMISI-BÉLOMBÉ 5</p> <p>The Structure of [(<i>tert</i>-C₄H₉)₃PI][W(CO)₄I₃] – a Contribution on the Acceptor Properties of Iodophosphonium Ions (In German) N. KUHN, R. JÜSCHKE, W.-W. DU MONT, M. BÄTCHER, D. BLÄSER, and R. BOESE 9</p> <p>Photoionization and Ion Fragmentation of SF₄ (In German) H.-W. JOCHIMS, E. RÜHL, and H. BAUMGÄRTEL 13</p> <p>Photoionization Mass Spectra of Methyl(trifluoromethyl)sulfan CH₃SCF₃ (In German) G. HAGENOW, H.-W. JOCHIMS, J. SAWATZKI, R. MINKWITZ, and H. BAUMGÄRTEL 17</p> <p>Photoion Spectroscopy of Sulfurchloridopentafluoride SF₅Cl, the Ionization Potential of Sulfurpentafluoride SF₅ (In German) H. BAUMGÄRTEL, H.-W. JOCHIMS, E. RÜHL, O. LÖSKING, and H. WILLNER 21</p> <p>Dithiocarbimates from Sulfonamides, Part 1: Preparation and X-Ray Crystal Structures of K₂[S₂C=N-SO₂-C₆H₅]·2H₂O and K₂[S₂C=N-SO₂-C₆H₄-Cl]·2H₂O H.-U. HUMMEL and U. KORN 24</p> <p>Dithiocarbimates from Sulfonamides, Part 2: Preparation and X-Ray Crystal Structures of (PPh₄)₂[Ni(S₂C=N-SO₂-Ph)₂] and (PPh₄)₂[Ni(S₂C=N-SO₂-C₆H₄-Cl)₂]·2H₂O H.-U. HUMMEL and U. KORN 29</p>	<p>New Transition Metal Complexes with the Ligand Me₂S(O)=NPPh₂=N- (In German) H. W. ROESKY, F. SCHRUMPF, and M. NOLTE-MEYER 35</p> <p>Dibenzoylmethane Reaction with Dichlorophenylphosphine: Oxygen Transfer from Carbon to Phosphorus <i>via</i> a Defined C₂PO₃ Phosphorane W. V. DAHLHOFF, K. M. TABA, and R. MYNOTT 41</p> <p>Borylation of Sulfamides, Sulfonimines and Sulfonediimines (In German) W. EINHOLZ, G. FREY, and W. HAUBOLD 47</p> <p>¹³C and ¹⁵N NMR Spectroscopic Study of Some Pentacarbonylchromium-Aminophosphane Complexes (In German) B. WRACKMEYER, K. SCHAMEL, and M. HERBERHOLD 55</p> <p>Phase Diagrams of Methylhalogenosilanes with Pyridine and Lutidine (In German) K. HENSEN and M. DRÄBING 63</p> <p>Reactions of Sodium Complexes of Aromatic Ethers with Dichloro(diorganylamino)boranes (In German) W. MARINGELE and A. MELLER 67</p> <p>Vibrational Spectrum of the Cluster Compound Nb₆F₁₅ (In German) G. KLICHE and H. G. VON SCHNERING 74</p> <p>Synthesis of Water Soluble Tetrairidium Clusters Suitable for Heavy Atom Labelling of Proteins W. JAHN 79</p> <p>Chemistry on Rigid Interfaces, 9. Properties and Behaviour of Onium Group Modified Aerosils. Some Examples of Interparticular Reactions (In German) L. HORNER and W. ROTH 83</p> <p>The Synthesis of Some Cyclopentadienyliron-Indium Complexes N. C. NORMAN and P. M. WEBSTER 91</p>
--	--

Notes

Syntheses of Dicyclopentadienyl-Titanium(IV) Substituted Carbodiimides (In German)

H. PLENIO and H. W. ROESKY 94

Synthesis and Structure of 2,4,6,8-Tetrakis(diisopropylamino)2,4,6,8-tetrabora-tricyclo-[3.3.0.0^{3,7}]-octane (In German)

A. KRÄMER, H. PRITZKOW, and W. SIEBERT 96

Synthesis and Silica Gel Promoted Rearrangement of 5-Methylthio-3-carbo-*t*-butoxy-pent-3-en-2-one

P. BAŁCZEWSKI and M. MIKOLAJCZYK 99

Phase Diagrams of Aluminium Halide-Pyridinium Halide Systems, III. Determination of the Phase Diagrams Aluminium Bromide-Pyridinium Iodide and Aluminium Chloride-Pyridinium Bromide (In German)

G. SEEMANN and K. HENSEN 102

Contents of Number 2

Original Communications

Synthesis and Structure of Trimeric 1,5-Bis(*p*-ethoxyphenyl)pentaazadienido-copper(I) – A Complex with Short Cu–Cu Contacts in a Linear Cu₃³⁺ Unit (In German)

R. SCHMID and J. STRÄHLE 105

Synthesis and Structure of μ -Bromo- μ -dioxo-bis-(phthalocyaninato-niobium(V))tribromide, [(PcNb)₂O₂Br]⁺Br₃⁻, a Dinuclear Phthalocyaninato Complex (In German)

F. GINGL and J. STRÄHLE 110

Synthesis and Crystal Structure of [Na-15-Crown-5][WF₅(NCl)] (In German)

A. GÖRGE, K. DEHNICKE, and D. FENSKE 117

Detection of the Isotopomeric *closo*-Hydrohexaborates ¹¹B_{*n*}¹⁰B_{6-*n*}H₆²⁻, *n* = 0–6, by Low Temperature Raman Spectroscopy (In German)

W. PREETZ and J. THESING 121

Chemistry of Polyfunctional Molecules, 104.

Gold-, Palladium- and Platinumchlorocomplexes of (±)-2-[N,N-Bis(2-diphenylphosphinoethyl)-amino]-tetrahydro-2*H*-1,3,2-oxazaphosphorine-2-oxide (In German)

J. ELLERMANN and N. WILL 127

Photochemical Splitting of a Polar Metal–Metal Bond by Metal to Metal Charge Transfer Excitation of [Ph₃PAu–Co(CO)₄] (In German)

A. VOGLER and H. KUNKELY 132

The Crystal Structure of [Ca(N₃)₂(H₂O)₂]·C₆H₁₄N₄ at 100 K (In German)

F. A. MAUTNER, H. KRISCHNER, and CH. KRATKY 135

Opening of Trinuclear Clusters by Diphosphino-methane Ligands (In German)

R. P. PLANALP and H. VAHRENKAMP 139

Photoredox Reactions of Hg(CN)₂/[Fe(CN)₆]⁴⁻ and [HgCo₂(CN)₁₀]⁶⁻ Induced by Inner-Sphere Metal to Metal Charge Transfer Excitation

H. KUNKELY, G. STOCHEL, and A. VOGLER 145

Tris(benzoyl-thiobenzoyl-methanato-O,S)indium, a Conformer of a Facial Isomer

V. D. GUPTA, A. K. MISHRA, H. NÖTH, and K. POLBORN 149

A Convenient Preparation of Bis(phosphorothioyl) Sulfides

S. MIN, H. ISHIHARA, T. MURAI, and S. KATO 153

Ruthenium Complexes with Diazadienes, IX. A New Chromophore from Two Diazadiene Ruthenium Units – Structure and Properties of [(CO)₂(DAD)CH₃Ru–RuCH₃(DAD)(CO)₂] (DAD = *ipr*–N=CH–CH=N–*ipr*) (In German)

H. TOM DIECK, W. ROHDE, and U. BEHRENS 158

Molecular and Crystal Structure of Two Cyclobuten-3,4-dione Derivatives: The Dithallium Salt of 1,2-Dicyanimino- (Tl₂CMCB) and the 1,2-Diodocyclobuten-3,4-dione (I₂CB)

B. LUNELLI and M. MONARI 169

Reactive E=C(*p*–*p*) π -Systems, XIX. F₃CP=C(H)F and F₃CP=C(D)F as Dienophiles (In German)

U. ALTHOFF, J. GROBE, D. LE VAN, and E.-U. WÜRTHWEIN 175

- On the Dynamic Structure Behaviour of the Dimethylamine–Carbon dioxide Complex (Dimcarb) (In German)
R. RADEGLIA, J. ANDERSCH, and W. SCHROTH 181
- Radical Ions, 81. ENDOR Spectroscopic Investigations of Radical Cations of Aromatic Organosulfur Compounds (In German)
H. BOCK, B. HIERHOLZER, and P. RITTMAYER 187
- Synthesis and Crystal Structure of the Amidinato Complex Ph–C(NSiMe₃)₂TeCl₃ (In German)
E. HEY, CH. ERGEZINGER, and K. DEHNICKE 205
- α -Aminoalkylation of Enamines with Iminium-tetrachloro-aluminates (In German)
N. RISCH and A. ESSER 208
- Organometallic Compounds with *o*-Phenylene Substituents, Part XVI. 2:1-Complexes of 2,3,7,8-Tetramethoxychalcogenanthrenes with Tetracyanoethene (In German)
P. BERGES, J. KUDNIG, G. KLAR, E. S. MARTÍNEZ, and R. D. CALLEJA 211
- Heterocyclic Seven-Membered Ring Compounds, XXXIV. A Simple Synthesis of 1-Benzoxepine and 1-Benzothiepine (In German)
H. HOFMANN and H. DJAFARI 220
- Chemistry on Rigid Surfaces, 11. Aerosils with Covalently Movable and Rigid Linked Fluorophors (In German)
L. HORNER, W. HALLENBACH, and M. VOGT 225
- Synthesis of 1-Benzoylpyrrolone Derivative and Related Compounds
A. A. A. ELBANNANY and L. I. IBRAHIM 233
- Notes*
- Synthesis and Structure of K₂Au₃, a New Phase in the System Potassium–Gold (In German)
P. KRIEGER-BECK, A. BRODBECK, and J. STRÄHLE 237
- Note on Carbonyl Derivatives with a Chiral Phosphorylhydrazine
E. V. DEHMLOW and CH. SAUERBIER 240
- The Space Group of (TTM-TTF)²⁺(AuCl₄⁻)₂ [TTM-TTF = Tetra(methylthio)tetrathiofulvalene]
P. G. JONES 243
- High Catalytic Activity of Vanadium(V) Oxo-Polymers for Oxidative Cleavage of Catechol
Y. NISHIDA and H. KIKUCHI 245
- Contents of Number 3
- Original Communications*
- Seleno-antimonates(V): Preparation and Crystal Structure of Na₃SbSe₄, K₃SbSe₄ and [Ba(en)₄]₂[Ba(en)₃](SbSe₄)₂ (In German)
B. EISENMANN and R. ZAGLER 249
- Polynuclear Mixed-Metal Complexes. Preparation and Structures of Complexes with the Cations [M^{II}{(OH)₂Co^{III}(en)₂}]₃⁵⁺, M = Ni, Zn, Mg (In German)
S. MÜLLER and U. THEWALT 257
- Preparation and Crystal Structure of NdSe_{1.9} (In German)
W. URLAND, P. PLAMBECK-FISCHER, and M. GRUPE 261
- Lithio-di-*tert*-butylfluorosilyl-*tert*-butylphosphane – Crystal Structure and Reactions (In German)
R. BOESE, D. BLÄSER, M. ANDRIANARISON, and U. KLINGEBIEL 265
- Reaction of Oxovanadium(V) Trichloride with *tert*-Butylamine and Silylated Derivatives (In German)
F. PREUSS, E. FUCHSLOCHER, E. LEBER, and W. TOWAE 271
- π -Olefin Iridium Complexes, XV. Cationic Bis(2,3-dimethylbutadiene)iridium-L Compounds with Various Donor Ligands L (In German)
J. MÜLLER, C. HÄNSCH, and J. PICKARDT 278
- Direct Synthesis of Organobromogermanes from Methylenebromide and Germanium/Copper Mixtures (In German)
H. SCHMIDBAUR and J. ROTT 285

- Dynamic Behaviour of Dimeric 1,2,3,4 λ^2 -Diazasilastannetidines and -plumbetidines in Solution – a Multinuclear NMR Study (In German)
B. WRACKMEYER, K. HORCHLER, HONG ZHOU, and M. VEITH 288
- Compounds of Subvalent Main Group Metal Cations with Dithiolates, Part 3. Crystal Structure of [As(C₆H₅)₄]₂[Pb(S₂C=C(CN)₂)₂] (In German)
H.-U. HUMMEL and H. MESKE 293
- Syntheses, Crystal Structure and Vibrational Spectra of Cs₃As₇ and Cs₃(NH₃)As₇ (In German)
M. SOMER, W. HÖNLE, and H. G. VON SCHNERING 296
- Crystal Structure of a Binuclear Copper(II) Complex with μ -Alkoxo and μ -Pyridonato Bridges. Effect of the Dihedral Angle on the Superexchange Interaction
Y. NISHIDA, M. MASUMOTO, and Y. MORI 307
- Transition Metal Complexes with Sulfur Ligands, XLII. [Mo(NO)(NR₂)(dtdt)]: Metal Amido Complexes with Rotationally Stable M–NR₂ Double Bonds (R = H, Me, Et; dtdt²⁻ = 2,3,8,9-Dibenzo-1,4,7,10-tetrathiadecane(2-)); Synthesis, Properties and X-Ray Structures (In German)
D. SELLMANN, G. PÖHLMANN, F. KNOCH, and M. MOLL 312
- Spectral and Thermal Studies on Some New Anionic Mixed Alkyldithiocarbonato-Oxinate Transition Metal Complexes
A. A. M. ALY and A. I. EL-SAID 323
- Donor/Acceptor Complexes from 1,3,5-Tris(dimethylamino)benzene with 1,2,3,4,5,6-Hexacyanobenzene (In German)
H. J. KELLER, R. NIEBL, G. RENNER, D. VON DER RUHR, A. K. KILIC, and D. SCHWEITZER 327
- Structure Investigation of Chiral Schiff Bases of 11-*cis*-Retinal (In German)
V. BUSS, V. HAAS, and U. WINGEN 333
- The Absolute Configuration of the Juglomycins (In German)
J. KRUPA, H. LACKNER, P. G. JONES, K. SCHMIDT-BÄSE, and G. M. SHELDRIK 345
- New Juglomycins (In German)
H. LESSMANN, J. KRUPA, H. LACKNER, and P. G. JONES 353
- Notes*
- Preparation of SH₃⁺AsF₆⁻ and SCl₃⁺SbF₆⁻ (In German)
R. MINKWITZ and V. GERHARD 364
- Trimethylphosphine Stabilized Monocyclopentadienyl Complexes of Niobium(III) and Tantalum(III) (In German)
H. G. ALT and H. E. ENGELHARDT 367
- Di-trichloroacetimide; IR Spectrum and Crystal Structure (In German)
U. PATT-SIEBEL, U. MÜLLER, P. KLINZING, and K. DEHNICKE 370
- Na₄OI₂ – a New Type of Alkali Metal Chalcogenide Halide (In German)
H. SABROWSKY, K. HIPPLER, and P. VOGT 373
- Contents of Number 4
- Original Communications*
- Contributions to the Chemistry of Phosphorus, 193. 1,2-Bis(di-*tert*-butylcyclotriphosphanyl)-3,4-di-*tert*-butylcyclotetraphosphane – a Novel P₁₀R₆ Structure Type (In German)
M. BAUDLER, L. DE RIESE-MEYER, and CH. WIATEREK 375
- Contributions to the Chemistry of Phosphorus, 194. Sodium Pentaphosphacyclopentadienide: Preparation from White Phosphorus and Sodiumdihydrogenphosphide (In German)
M. BAUDLER and D. OUZOUNIS 381
- Di- and Trinuclear Fluorooxoanions of Vanadium. Crystal Structures of Cs(NMe₄)[V₂O₂F₈(H₂O)] and (Na,K)(NMe₄)₂[V₃O₃F₁₂] (In German)
M. HILBERS, M. LEIMKÜHLER, and R. MATTES 383

- Di- and Trinuclear Fluoro-oxoanions of Molybdenum and Tungsten. Crystal Structures of $K_2(NMe_4)[Mo^V_2O_2F_9] \cdot H_2O$ and $(NMe_4)_2[Mo^{VI}_2O_4F_6(H_2O)]$ (In German)
M. LEIMKÜHLER, N. BUCHHOLZ, and R. MATTES 389
- From 1,5-Functional Trisiloxanes to $(SiO)_4$ -, $[Si(OSiN)_2Si]$ -, and $[O(SiOSi)_2N]$ -Rings (In German)
D. SCHMIDT-BÄSE and U. KLINGEBIEL 395
- X-Ray and Spectroscopic Investigation of Some Strontium and Zinc Substituted Calcium Fluoroapatites (In German)
M. C. APPELLA, M. E. TUTTOLOMONDO, and E. J. BARAN 402
- Regular Octahedral Coordination of As(III) in the Anion $[As_3Br_{12}]^{3-}$. Structural Correlation of the Antibonding Influence of the $As4s$ -Orbital in Bromoarsenates(III)
W. S. SHELDRIK and C. HORN 405
- Preparation and Vibrational Spectra of Fluoro-Chloro-Platinates(IV) Including Stereoisomers (In German)
W. PREETZ and P. ERLHÖFER 412
- Boron-Stabilized N,O-Carbenes. I. Triphenylboron Adducts of Siloxy- and Hydroxyalkyl Isocyanides and Spontaneous Formation of Ate-Ylids (In German)
W. P. FEHLHAMMER, H. HOFFMEISTER, H. STOLZENBERG, and B. BOYADJIEV 419
- Reactions of Complex Bound Ligands. XXXIX. Reactions of the Low Valent Azido Complexes $NEt_4[CpMn(CO)_2N_3]$ and $[CpFe(cdpe)N_3]$ with Electrophiles and 1,3-Dipolarophiles (cdpe = *cis*-1,2-Bis(diphenylphosphino)ethen) (In German)
D. SELLMANN, E. LICHT, M. MOLL, and F. KNOCH 429
- Novel Basic Ligands for the Homogenous Catalytic Methanol Carbonylation, XXI. Synthesis and Properties of (Ether-Phosphane) Platinum Complexes (In German)
E. LINDNER and R. SPEIDEL 437
- Syntheses and Crystal Structures of the Crown Ether Complexes.
 $[Li_3(12-Crown-4)_3O_2CCH_3][Cd(Se_4)_2]$, $\{[K(18-Crown-6)]_2[Hg(Se_4)_2]\}_2$, and $[Na(15-Crown-5)]NO_3$ (In German)
G. KRÄUTER, F. WELLER, and K. DEHNICKE 444
- New Cyclopentadienones from Sterically Demanding Inner Acetylenes and Dicobalt-octacarbonyl
E. V. DEHMLow and A. WINTERFELDT 455
- Metal Complexes of Biologically Important Ligands. L. Palladium(II), Platinum(II) and Copper(II) Complexes of α -Amino Acid-N-Glycosides and of Fructose-Amino Acids (Amadori-Compounds) (In German)
JINGTANG CHEN, TH. PILL, and W. BECK 459
- Polysulfonylamines. XV. Synthesis of N,N,N',N'-Tetramesyl Dicarboxylic Diamides. Cyclization of N,N,N',N'-Tetramesyl Succinic Diamide to γ -Dimesylamino- $\Delta^{\beta,\gamma}$ -butenolide (In German)
A. BLASCHETTE, K. LINOH, D. KOCH, and L. ERNST 465
- Structural Investigations of Co(III)- and Ni(II)-Complexes of Pyridine-2,6-di(monothiocarboxylic Acid) (In German)
U. H. W. HILDEBRAND and J. LEX 475
- Intramolecular Donor-Acceptor Interactions in N,N'-Dimethylurea Derivatives of Phosphorus (In German)
TH. KAUKORAT and R. SCHMUTZLER 481
- Heterocyclic Synthesis with Nitriles: A Novel Synthesis of Some Thiophene and Thieno[2.3-d]pyrimidine Derivatives, II
F. M. ABDELRAZEK 488
- Notes
- Synthesis and IR Spectrum of $[MoCl_4(NCl)]_2$ (In German)
A. FRANKENAU and K. DEHNICKE 493
- Synthesis and Crystal Structure of the Cyclic Hydrazido Complex $\{Fe_2Cl_4[(NSiMe_3)(CPh)]_2N_2\}$ (In German)
W. HILLER, E. HARTMANN, and K. DEHNICKE 495

- AgNb₃O₈-II, a High-Pressure Phase with a Novel Tunnel Structure (In German)
K.-J. RANGE and M. WILDENAUER 499
- Preparation and Characterization of Some Unsymmetrical Chlorodiorganophosphines RR'PCl (In German)
JUNG SU HAN and W. WOLFSBERGER 502
- Contents of Number 5
- Original Communications*
- Phase Relations in the System NaIn-Sn and the Crystal Structures of the Intermediate Compounds NaInSn₂ and NaInSn₄ (In German)
W. BLASE, G. CORDIER, R. KNIEP, and R. SCHMIDT 505
- Electron Rich Olefins, 3. Formation of the First N,N'-Persilylated 1,4-Diaminoethene *via* a 1,2,3-Triazoline(4)-Intermediate with 8 Cyclically Conjugated π Electrons and 3 Neighbouring N Electron Pairs (In German)
CH. BESSENBACHER and W. KAIM 511
- The Crystal Structures of Hydrates of Strontium and Barium Hexacyanoferrate(III) with Hexamethylenetetramine. Structural Model for Adducts of the Hexacyanoferrates of Alkaline and Alkaline Earth Metals with Hexamethylenetetramine (In German)
H.-J. MEYER and J. PICKARDT 519
- The Molecular Nature of the Hydrophilic Sulfur Prepared from Aqueous Sulfide and Sulfite (Selmi Sulfur Sol)
R. STEUDEL, TH. GÖBEL, and G. HOLDT 526
- Reaction of [η^5 -CpMCl₄] (M = Nb, Ta) with E(SiMe₃)₂ (E = S, Se). The Crystal Structures of [Cp₃Ta₆S₁₀][TaSCl₅], [Cp₃Ta₃S₇Cl₂], [Cp₄Ta₄S₁₃] and [Cp₃Nb₃Se₅Cl₂] (In German)
D. FENSKE and P. G. MAUÉ 531
- Influence of Decreasing Solvent Polarity (Dioxane-Water Mixtures) on the Stability of Metal Ion Complexes Formed with Phosphate Monoesters
G. LIANG, N. A. CORFÙ, and H. SIGEL 538
- Preparation and Structures of α,β -Unsaturated Aliphatic Diazenes (In German)
H. W. ROESKY, U. OTTEN, R. HERBST, and M. NOLTEMEYER 543
- Synthesis and Crystal Structure of 2-Trimethylsilyl-1,3-bis-trimethylsilylimino-1,3-dihydro-isoindole and the Crystal Structure of Hexakis(trimethylsilyl)-1,4-benzdiamidine (In German)
F. WELLER, F. SCHMOCK, and K. DEHNICKE 548
- Crystal Growth in Gels and X-Ray Characterization of Polymeric 1:1-Complexes of CuBr₂ and CuCl₂ with Pyrazine (In German)
TH. FETZER, A. LENTZ, and T. DEBAERDEMAEKER 553
- Photophysics of Ceramic Luminophores. Zeolite-Based Luminophores of the Types Zn₂SiO₄:Mn and (CdO)₂B₂O₃:Mn
K. HESSE, G. GLIEMANN, A. KISS, P. KLEINSCHMIT, and W. VÖLKER 557
- Crystal Structure of the Dimeric Triethylarsine-Arsenictrichloride Adduct, Dimer [Et₃As \times AsCl₃]₂: Synthesis, Molecular and Crystal Structure (In German)
G. BAUM, A. GREILING, W. MASSA, B. C. HUI, and J. LORBERTH 560
- Stereochemistry of 2,6-Dipyridine Substituted N-Benzyl-4-piperidone Mono- and Dicarboxylates and of the Corresponding Reduction Products
U. HOLZGRABE, B. PIENING, K.-F. HESSE, H.-D. HÖLTJE, and M. WORCH 565
- Solid State Structure of 2,2,4,4,6,6-Hexa(β -naphthyl-oxo)cyclophosphazatriene and Dipole Moments of Hexa(aryloxo)cyclophosphazatrienes
G. BANDOLI, U. CASELLATO, M. GLERIA, A. GRASSI, E. MONTONERI, and G. C. PAPPALARDO 575
- Aminations with O-Diphenylphosphinylhydroxylamine. A Critical Evaluation
G. SOSNOVSKY and K. PURGSTALLER 582
- 2,2-Diethoxy-1-ethenediazonium Hexachloroantimonate: A Versatile Building Block for the Synthesis of 5- and 6-Membered N-Heterocycles. Crystal and Molecular Structure of 5'-Phenyl-3'-(2-phenyl-6H-1,3,4-oxadiazine-5-yl)spiro[isoben-

- zofuran-1(3H),2'(3'H)-[1,3,4]-oxadiazol]-3-one
(In German)
R. W. SAALFRANK, B. WEISS, U. WIRTH, K. PETERS, and H. G. VON SCHNERING 587
- Degradation of Lactic Acid and Pyruvic Acid in Belousov-Zhabotinskii Reactions
R. BLUME, D. WIECHOCZEK, H. MEIER, and F. WEDEKIND 598
- Notes*
- Crystal Structure of $[\text{Et}_4\text{N}][\text{PBr}_4]$. Structural Correlation for Halogenophosphates(III) (In German)
W. S. SHELDRIK and J. KIEFER 609
- Cyclotriphosphazene-2-spiro-3'-cyclo-di[phosphadiazane] - A Spiro Compound from Hexachlorocyclotriphosphazene and Dihyrazidothiophosphoric Acid *o*-Phenylester (In German)
U. ENGELHARDT and U. DIEFENBACH 612
- The Synthesis and Crystal Structure of $(R^*, R^*)-(\pm)-[(\eta^5\text{-C}_5\text{H}_5)\{1,2\text{-C}_6\text{H}_4(\text{PMePh})_2\}\text{Fe}(\text{PCl}_3)_2\text{Cl} \cdot 2\text{MeCN}$
E. HEY, S. B. WILD, S. G. BOTT, and J. L. ATWOOD 615
- Contents of Number 6
- Original Communications*
- Preparation and Vibrational Spectra of $^{35}\text{Cl}/^{37}\text{Cl}$ Labelled Fluoro-Chloro-Platinates(IV) (In German)
P. ERLHÖFER and W. PREETZ 619
- Contributions to the Chemistry of Phosphorus, 196. Synthesis and Properties of the Organotris(phosphino)silanes $\text{RSi}(\text{PH}_2)_3$ (R = Me, Et, *i*-Pr, Ph) (In German)
M. BAUDLER, G. SCHOLZ, and W. OEHLERT 627
- Manganese(II) Complexes with the Tetradentate Nitrogen Ligand $\text{C}_{12}\text{H}_{22}\text{N}_6(\text{L})$: Synthesis of $[\text{MnX}_2\text{L}]$ (X = Cl, Br, I, NCS), Crystal Structures of $[\text{MnCl}_2\text{L}]$ and $[\text{MnBr}_2\text{L}]$ (In German)
P. STOLZ, W. SAAK, H. STRASDEIT, and S. POHL 632
- Studies on the Polypseudohalides, VI. Preparation and Crystal Structure of $\text{Na}[\text{I}(\text{CN})_2] \cdot 2\text{H}_2\text{O}$ (In German)
K.-F. TEBBE and N. KRAUSS 637
- Preparation and Spectroscopic Characterization of *trans*- $\text{Fe}(\text{CO})_3\text{L}^1\text{L}^2$ ($\text{L}^1, \text{L}^2 = \text{Phosphine or Phosphite}$)
H. INOUE, T. KUROIWA, T. SHIRAI, and E. FLUCK 641
- Cluster Synthesis by Photolysis of R_3PAuN_3 , III. Synthesis of $[(\text{Ph}_3\text{PAu})_5\text{Fe}(\text{CO})_3]\text{PF}_6$ and $\text{Ru}_3(\text{CO})_{10}(\mu\text{-AuPPh}_3)(\mu\text{-NCO})$ (In German)
G. BEUTER and J. STRÄHLE 647
- A ^{15}N NMR Study of Some Trimethylstannylhydrazines (In German)
B. WRACKMEYER, TH. GASPARIS-EBELING, and H. NÖTH 653
- The Structures of Indolyl(alkoxy)carbenium Tetrafluoroborates: A New Class of Highly Stabilized Carbenium Ions
U. PINDUR, L. PFEUFFER, C. FLO, W. MASSA, and K. SEITZ 659
- Isonitrile Substituted Half Sandwich Complexes of Wolfram(IV) (In German)
A. C. FILIPPOU and W. GRÜNLEITNER 666
- Empirical Parameters of Lewis Basicity of Binary Solvent Mixtures, Part II. Mixtures with Water
P. K. WRONA, T. M. KRYGOWSKI, and U. ZIELKOWSKA 673
- Formation and NMR Spectroscopic Characterization of the Fluorophosphonium Cations, $\text{PH}_{4-n}\text{F}_n^+$ ($n = 1-4$) (In German)
R. MINKWITZ and A. LIEDTKE 679
- Studies on Alkyl Heterocyclic Aromatic Compounds: New Routes for the Synthesis of Polyanaphthalenes
M. H. ELNAGDI, F. A. M. A. AAL, E. A. A. HAFEZ, and Y. M. YASSIN 683
- Preparation of *p*-Chloro-Substituted *N,N'*-Dimethylurea-Bridged Diphosphorus Compounds, their Dehalogenation with Oxalic Acid Bis(trimethyl-

silyl) Ester and Subsequent Oxidation with Tetrachloro- <i>o</i> -benzoquinone (In German)	690	Structural and Transport Studies for Ternary Graphite Intercalated Phases (CoCl ₂ , AlCl ₃)	761
R. VOGT and R. SCHMUTZLER		P. PERNOT and R. VANGELISTI	
Surface Reactions, 9. Dehydrohalogenation of Halohydrocarbons at Raney Nickel (In German)	699	Polarographic Investigations for the Determination of the Stability of Metal-Protein Bonds (In German)	767
H. BOCK and H. P. WOLF		H. REINECKE, L. DUNEMANN, and G. SCHWEDT	
Contents of Number 7		Electrochemical Investigations on Graphite Salts with HNO ₃ , HClO ₄ , HReO ₄ and Halogenated Acetic Acids (In German)	772
<i>Original Communications</i>		P. SCHARFF	772
The Jahn-Teller Distortion in the Crystal Structures of the Disodium-Tetrafluorometallates Na ₂ CuF ₄ and Na ₂ CrF ₄ (In German)	715	Dimeric Triazenido and Pentaazadienido Complexes of Monovalent Silver. Synthesis and Structure of [Ag(MeOC ₆ H ₄ N ₃ C ₆ H ₄ OMe)] ₂ · 2/3 Pyridine, [Ag(MeOC ₆ H ₄ N ₃ C ₆ H ₄ OMe)] ₂ and [Ag(EtOC ₆ H ₄ N ₃ C ₆ H ₄ OEt)] ₂ · Pyridine (In German)	778
D. BABEL and M. OTTO		E. HARTMANN, R. SCHMID, and J. STRÄHLE	
Synthesis and Structure of the Graphite Intercalation Compounds of Mercuric Chloride (In German)	721	Structural Chemistry of Unsaturated Silicon Compounds: Crystal and Molecular Structures of the Stable Silaneimine 'Bu ₂ Si=N-Si'Bu ₃ and of Silaneimine Donor Adducts (Donor = Tetrahydrofuran, Benzophenone) (In German)	786
P. BEHRENS, M. ALIDOOSTI, F. SCHULZ, and W. METZ		G. REBER, J. RIEDE, N. WIBERG, K. SCHURZ, and G. MÜLLER	
Anodic Surface and Bulk Oxidation of Graphitic Materials in Neutral and Basic Aqueous Solutions (In German)	729	Silaheterocycles: Molecular Structure of a 3-Oxa-2,4,6,7-tetrasilabicyclo[3.1.1]heptane (In German)	796
J. O. BESENHARD, J. JAKOB, U. KREBBER, P. MÖLLER, R. F. SAUTER, A. KURTZE, N. KANANI, H. MEYER, J. K. H. HÖRBER, and A. D. JANNAKOUAKIS		G. REBER, J. RIEDE, N. WIBERG, G. WAGNER, and G. MÜLLER	
Complexation in TiCl ₃ and Chlorothallate(III) Melt Systems (In German)	736	(Dimethylphosphito-P){tris[2-(diphenylphosphino)ethyl]phosphine-P',P'',P'''}platinum(II)-chloride: Synthesis and Structural Characterization	800
W. BROCKNER, V. ALEXIOU, and M. SOMER		P. BRÜGGELLER, TH. HÜBNER, and A. GIEREN	
Fluorescence Measurements on the Photooxidation of Poly(ethyleneterephthalate) Films and a Photoselective Effect	745	5β,6β-Epoxidation of 3β-Cholesteryl Acetate and its Analogues	806
M. HENNECKE, I. KECK, E. LEMMERT, and J. FUHRMANN		L. R. GALAGOVSKY, G. BURTON, and E. G. GROS	
The Semiconductor-Metal Transition in Pyrochlores of the System Ln _{2-x} Cu _x Ru ₂ O _{7-z} (Ln = Pr, Sm, Eu, Gd, Dy) (In German)	750	Catechoyl-Dipeptides as Leucine Aminopeptidase Inhibitors	811
G. MAYER-VON KÜRTHY, W. WISCHERT, and S. KEMMLER-SACK		Ł. NAKONIECZNA, J. J. PASTUSZAK, and A. CHIMIĄK	
Graphite Compounds with Chlorine Trifluoride	755		
R. PENTENRIEDER and H. P. BOEHM			

- Carnivora: The Amino Acid Sequence of the Adult European Polecat (*Mustela putorius*, Mustelidae) Hemoglobins
 A. AHMED, M. JAHAN, G. BRAUNITZER, and H. PECHLANER 817
- Intramolecular Cycloaddition Reactions with Iso-benzofurans VII. Synthesis of rac. Thiafarfugin A, a Thiophene Analogue of a Naturally Occurring Furanosquiterpene (In German)
 A. SCHÖNING and W. FRIEDRICHSEN 825
- Synthesis of Bicyclic and Tricyclic Enones *via* Regioselective Dialkylation of Cyclic 1,3-Diketone-dimethylhydrazones with 4-Chlorobutane-2-one
 A. S. DEMIR and D. ENDERS 834
- 1-Acceptor Substituted Vinamidinium Salts: Stability and Reactivity (In German)
 E. BACHER, R. GOMPPER, R. MERTZ, and H.-U. WAGNER 839
- Notes*
- Preparation and Crystal Structure of Cs₄Sn₂Se₆ (In German)
 W. S. SHELDRIK and H. G. BRAUNBECK 851
- Crystal and Molecular Structure of 2,4-Bis(diisopropylamino)-3-phenyl-1,3,2,4-thiazadiboretidine (In German)
 C. D. HABBEN and M. NOLTEMEYER 853
- Crystal Structure of 1,1-Dichloro-3,5-diphenyl-4-H-1,2,4,6-λ⁴-selenatriazine, SeCl₂C₂N₃H(C₆H₅)₂ (In German)
 D. FENSKE, CH. ERGEZINGER, and K. DEHNICKE 857
- Cyclophanes, XXX. The Crystal Structure of [2.4]Paracyclophane at -95 °C
 P. G. JONES, Z. PECHLIVANIDIS, and H. HOPF 860
- Reactions with Dimethyl Carbonate, 5. Methylation of the Pyrimidine Bases of Nucleic Acids (In German)
 H. JANSEN IN DE WAL, M. LISSEL 863
- Chirality Caused by Hindered Rotation: Isolation of Optically Active Naphthylamines (In German)
 TH. HERBST and G. P. SCHIEMENZ 866
- Contents of Number 8
- Original Communications*
- Distribution and Valence of the Cations in Spinel Systems with Iron and Vanadium, VI. Lattice Constants, Mössbauer Spectra and Electronic Properties of the Solid Solution ZnFeVO₄-Fe₂VO₄ (In German)
 E. RIEDEL, A. OSTERMANN, and J. KÄHLER 869
- Distribution and Valence of the Cations in Spinel Systems with Iron and Vanadium, VII. The Non-stoichiometric Spinel FeV₂O₄ (In German)
 E. RIEDEL and J. KÄHLER 875
- Synthesis of a New Chiral Phosphine Ligand (In German)
 D. FENSKE and K. MERZWEILER 879
- Synthesis of New Optically Active Rh-Complexes: The Crystal Structure of [(5S)-3,4-Bis(diphenylphosphino)-5-menthoxy-2(5H)-furanone](1,5-cyclooctadiene)rhodium-hexafluorophosphate (In German)
 D. FENSKE and K. MERZWEILER 884
- Synthesis, IR Spectrum, and Crystal Structure of the Amidinato Complex [Na(15-Crown-5)]-[Ph-C(NSiMe₃)₂SnCl₃F] (In German)
 J. D. KILDEA, W. HILLER, B. BORGEN, and K. DEHNICKE 889
- On the Complex Chemistry of the Alkali Metals: The Crystal Structure of RbLiS (In German)
 H. SABROWSKY, K. HIPPLER, R.-D. HITZBLECK, ST. SITTA, A. THIMM, P. VOGT, and R. WORTMANN 893
- Hexacyanomanganates(III) with Cryolite Type Structure: Cs₂NaMn(CN)₆ and Cs₂KMn(CN)₆ (In German)
 B. ZIEGLER, R. HAEGELE, and D. BABEL 896
- Substitution Reactions at the N-Chloronitreno Group of [WCl₄(NCl)]₂. The Crystal Structures of [CH₃CN-WCl₄(NSMe)] and [WNCl₃·NC-CH₃]₄ (In German)
 A. GÖRGE, U. PATT-SIEBEL, U. MÜLLER, and K. DEHNICKE 903

- Formation and Structure of Bis(2,6-dimethoxyphenyl)nitramine, $[2,6-(\text{MeO})_2\text{C}_6\text{H}_3]_2\text{NNO}_2$ (In German)
L. HEUER, R. SCHMUTZLER, and D. SCHOMBURG 911
- Boron Stabilized N,O-Carbenes, II. X-Ray Structure of (*trans*-4,5-Dimethyloxazolidin-2-ylidene)triphenylboron and N-Alkylations (In German)
W. P. FEHLHAMMER, H. HOFFMEISTER, B. BOYADJIEV, and TH. KOLREP 917
- Valence Force Constants of N-Benzylideneanilines
K. FIGUEROA A., R. PEÑA C., and M. M. CAMPOS-VALLETTE 923
- Barium Hydroxide Halides. Crystal Structure and Vibrational Spectra of $\text{Ba}[\text{O}(\text{H},\text{D})]\text{X} \cdot 2(\text{H},\text{D})_2\text{O}$ (X = Cl, Br) (In German)
H. D. LUTZ, TH. KELLERSOHN, and K. BECKENKAMP 928
- Syntheses and Structure Analyses of Iodocuprates(I). X. $[\text{Co}(\text{cp})_2]_2[\text{CuI}_3]$ and $[\text{Co}(\text{cp})_2][\text{Cu}_2\text{I}_3] = 1/9\{[\text{Co}(\text{cp})_2]_9[\text{Cu}_6\text{I}_{11}]^2\{(\text{Cu}_6\text{I}_8)_2\}$ (In German)
H. HARTL and I. BRÜDGAM 936
- Synthesis, Structure, and Thermal Behaviour of Phosphorothionic Triamide $\text{SP}(\text{NH}_2)_3$ (In German)
W. SCHNICK 942
- Thiobenzamide-thiobenzimide-bromo-copper(II), $[\text{Cu}(\text{PhCSNH}_2)(\text{PhCSNH})\text{Br}]_2$ (In German)
P. SOUZA, A. ARQUERO, A. CARCÍA-ONRUBIA, V. FERNÁNDEZ, A. M. LEIVA, and U. MÜLLER 946
- Studies on Condensed Pyrazoles. A New Route for Synthesis of Pyrazolo[4,3-c]pyrazoles
M. H. ELNAGDI, A. H. H. ELGHANDOUR, K. U. SADEK, and M. M. M. RAMIZ 951
- Effect of Urea and Organic Solvents on the Mitochondrial F_1 ATPase
G. DREYFUS and L. DE MEIS 955
- Peptide Free-Radicals: The Reactions of OH Radicals with Glycine Anhydride and its Methyl Derivatives Sarcosine and Alanine Anhydride. A Pulse Radiolysis and Product Study
O. J. MIEDEN and C. VON SONNTAG 959
- On the Stereochemistry of Pterocarpanoids – a Theoretical Study (In German)
A. SCHÖNING and W. FRIEDRICHSEN 975
- Synthesis and Activity of Juvenile Hormone Analogues (JHA), Part II
J. B. RODRIGUEZ, E. G. GROS, and A. M. STOKA 983
- Notes
- Chiral Ruthenium Halfsandwich Complexes of Sulfur Monoxide and Sulfur Dioxide (In German)
W. A. SCHENK and U. KARL 988
- Refinement of the Crystal Structures of CuTe_2Br and CuTe_2I
W. MILIUS 990
- Nucleophilic Addition of Alkoxide to a Cationic Ruthenium Sulfur Dioxide Complex (In German)
W. A. SCHENK and U. KARL 993
- Replacement of Nitrite by Bromide Anions in Na_3NO_3 (In German)
M. JANSEN and W. MÜLLER 996
- Contents of Number 9
- Original Communications
- Synthesis and Crystal Structure of N,N'-Bis(trimethylsilyl)benzamidinato-dichlorogold, $\text{Ph}-\text{C}(\text{NSiMe}_3)_2\text{AuCl}_2$ (In German)
W. HILLER, J. STRÄHLE, A. ZINN, and K. DEHNICKE 999
- Synthesis and Crystal Structure of the Imido Complex $\{\text{TaCl}_4\text{NC}(\text{Ph})[\text{N}(\text{SiMe}_3)_2]\}_2 \cdot 2\text{CH}_2\text{Cl}_2$ (In German)
K. MERZWEILER, D. FENSKE, E. HARTMANN, and K. DEHNICKE 1003
- Synthesis and Crystal Structure of Europium(III)-diacetatotriaquo-chloride, $[\text{Eu}(\text{CH}_3\text{COO})_2(\text{H}_2\text{O})_3]\text{Cl}$ (In German)
TH. SCHLEID and G. MEYER 1007

- The Crystal Structure of $\text{Na}_3\text{Ga}_8\text{Sn}_3$ and the Interpretation of its Chemical Bonding According to Wade's Rules and the Zintl Concept (In German)
W. BLASE and G. CORDIER 1011
- Transition Metal Complexes with Sulfur Ligands, XLVI. Zn, Cd, Hg, Sn, Pb, Bi and Ti Complexes with the Bi- and Tetradentate Thiolato Ligands $^{\text{bu}}\text{S}_2^{2-} = 3,5\text{-Di}(t\text{-butyl})\text{benzene-1,2-dithiolate}(2-)$, $^{\text{S}}_4^{2-} = 1,2\text{-Bis}(2\text{-mercaptophenylthio})\text{ethane}(2-)$ and $^{\text{bu}}\text{S}_4^{2-} = 1,2\text{-Bis}(3,5\text{-di}(t\text{-butyl})\text{-2-mercaptophenylthio})\text{ethane}(2-)$ (In German)
D. SELLMANN, G. FREYBERGER, and M. MOLL 1015
- Proton-Induced Coupling of one *tert*-Butylisonitrile with one Phenylcarbyne Ligand at Tungsten (In German)
A. C. FILIPPOU and W. GRÜNLEITNER 1023
- New Compounds Ag_2HgMX_4 with the Wurtzstannite Type Structure (In German)
H. HAEUSELER and M. HIMMICH 1035
- Tetraphenylphosphonium Hexachlorodizincate and Hexachlorodicadmate, $(\text{PPh}_4)_2\text{Zn}_2\text{Cl}_6$ and $(\text{PPh}_4)_2\text{Cd}_2\text{Cl}_6$ (In German)
J. H. WILHELM and U. MÜLLER 1037
- Stereoselective Synthesis of a Phenylphosphido-Bridged Dimetallic Complex: Crystal and Molecular Structure of $[(\text{R}^*, \text{R}^*), (\text{R}^*)]-(\pm)-[(\eta^5\text{-C}_5\text{H}_5)\{1,2\text{-C}_6\text{H}_4(\text{PMePh})_2\}\text{FePPh}\{\text{Cr}(\text{CO})_5\}] \cdot 2\text{H}_2\text{O} \cdot 0.5\text{CH}_2\text{Cl}_2 \cdot 0.5\text{C}_4\text{H}_8\text{O}$
E. HEY, A. C. WILLIS, and S. B. WILD 1041
- Li_2ZnI_4 , the First Olivine Type Iodide (In German)
H. D. LUTZ and A. PFITZNER 1047
- Aliphatic Bis(acyl) Selenides – Synthesis and Characterization
H. KAGEYAMA, H. TSUTSUMI, T. MURAI, and S. KATO 1050
- ^{127}I , ^{185}Re and ^{187}Re Solid State NMR Measurements on $(\text{CH}_3)_4\text{AsIO}_4$ and $(\text{CH}_3)_4\text{AsReO}_4$
M. GROMMELT and P. K. BURKERT 1053
- Interconversions between Vinylidene and Alkyldyne Bridged Trinuclear Clusters (In German)
W. BERNHARDT, H.-TH. SCHACHT, and H. VAHRENKAMP 1060
- Cyclic Diazastannylenes, XXX. Symmetrically and Asymmetrically Substituted Germane- and Stannanediyls with Amide, Alcoholate and Thiolate Ligands, Part I (In German)
M. VEITH, P. HOBEIN, and R. RÖSLER 1067
- Cyclopentadienyldifluorophosphine and its Homologues as Ligands in *cis*-Dichloroplatinum(II) Complexes – Structure of *cis*- $(\text{C}_5\text{Me}_5\text{PF}_2)_2\text{PtCl}_2$ and *cis*- $(\text{C}_9\text{H}_7\text{PF}_2)[(\text{C}_9\text{H}_7)_3\text{P}]\text{PtCl}_2$ ($\text{C}_5\text{Me}_5 = \text{Pentamethylcyclopentadienyl}$, $\text{C}_9\text{H}_7 = \text{Indenyl}$) (In German)
L. HEUER, U. K. BODE, P. G. JONES, and R. SCHMUTZLER 1082
- Bioinorganic Model Complexes for Metalloproteins of Iron(III): Syntheses, Crystal Structures, and Magnetism of the Binuclear Complexes $[\text{L}_2\text{Fe}^{2\text{III}}(\mu\text{-O})(\mu\text{-SO}_4)_2] \cdot 3\text{H}_2\text{O}$ and $[\text{L}_2\text{Fe}^{2\text{III}}(\mu\text{-O})(\mu\text{-SO}_3)_2] \cdot 5/3\text{NaClO}_4 \cdot (\text{H}_2\text{O})_{3,67}$ ($\text{L} = \text{N}, \text{N}', \text{N}''\text{-Trimethyl-1,4,7-triazacyclononane}$) (In German)
K. WIEGHARDT, ST. DRÜEKE, PH. CHAUDHURI, U. FLÖRKE, H.-J. HAUPT, B. NUBER, and J. WEISS 1093
- Photochemical Studies, 55. Photodimerization of Nootkatone in Crystalline State (In German)
J. REISCH, N. EKIZ-GÜCER, and M. TAKÁCS 1102
- Amphiphilic Carbohydrate-Based Mesogens, 4. Synthesis of a Homologous Series of Mesogenic 1-*O*-*n*-Alkyl-*D*-mannitols
W. V. DAHLHOFF 1105
- Conformation of Anthranilic Acid Peptides: Crystal Structure of *tert*-Butyloxycarbonyl-Anthranilic-Acid-Glycin-Methyl-Ester and Semi-Empirical (AM1) Description of the Ramachandran Map (In German)
M. FEIGEL, G. LUGERT, J. MANERO, and M. BREMER 1109
- Assignment of ^1H NMR Spectra of Depsides, Depsidones, Depsones and Dibenzofurans from Lichens by NOE Difference Spectroscopy (In German)
J. JAKUPOVIC and S. HUNECK 1117
- One Pot Synthesis of Methyl 3-Methyl-4H-1,4-benzothiazine 2-carboxylates
R. R. GUPTA, S. K. JAIN, V. GUPTA, and R. K. RATHORE 1124

- Synthesis and Ferroelectric Properties of 2,5-Diphenylpyrimidines with Different α -Fluorocarboxylic Acids (In German)
J. BÖMELBURG, G. HEPPKE, and A. RANFT 1127
- Studies on the Chemistry of Isoindoles and Isoindolenines, XXXV. 1-Alkoxy-2-alkyl-2H-isoindoles – *o*-Quinonoid Hetarenes with Unsymmetric Structure (In German)
R. P. KREHER, H. HENNIGE, F. JELITTO, and J. PREUT 1132
- Notes*
- Triorganoantimony Compounds as Ligands in Iron Complexes (In German)
M. WIEBER and H. HÖHL 1149
- Preparation and Crystal Structure of $[\text{H}_3\text{N}(\text{CH}_2)_3\text{NH}_3]\text{SbCl}_5$ (In German)
A. DU BOIS and W. ABRIEL 1151
- Contents of Number 10
- Original Communications*
- $[\text{Na-15-Crown-5}]_2[\text{ZrF}_2\text{Cl}_4]$ and $(\text{PPh}_4)_2[\text{ZrCl}_6] \cdot 2\text{CH}_2\text{Cl}_2$; Syntheses, IR Spectra, and Crystal Structures (In German)
E. HARTMANN, K. DEHNICKE, D. FENSKE, H. GOESMANN, and G. BAUM 1155
- On the Reduction of Alkyne Complexes of Molybdenum and Tungsten in High Oxidation States. The Crystal Structure of $\text{MoCl}_3(\text{THF})_3$ (In German)
P. HOFACKER, C. FRIEBEL, K. DEHNICKE, P. BÄUML, W. HILLER, and J. STRÄHLE 1161
- Contributions to the Chemistry of Phosphorus, 201. Pentaethylcyclopentaphosphane Monosulfide, $(\text{PEt})_5\text{S}$ – Preparation and Structure Determination by ^{31}P NMR Spectroscopy (In German)
M. BAUDLER and P. KOCH 1167
- f-Element Complexes with Chelating Sulfur-Nitrogen-Ligands: Synthesis and Structure of $[\text{PhS}(\text{NSiMe}_3)_2]_2\text{UCl}_2$ (In German)
F. KNÖSEL, M. NOLTEMAYER, and F. T. EDELMANN 1171
- π -Complexes of *p*-Block Elements:
 $[(\eta^6\text{-C}_6\text{Me}_6)\text{Sn}(\text{AlCl}_4)_2]_2 \cdot 3\text{C}_6\text{H}_6$ – a Dimeric Coordination Compound of Hexamethylbenzene with $\text{Sn}(\text{AlCl}_4)_2$
H. SCHMIDBAUR, TH. PROBST, O. STEIGELMANN, and G. MÜLLER 1175
- 1,2- and 1,1-Diborylalkenes (In German)
W. SIEBERT, M. HILDENBRAND, P. HORNBACH, G. KARGER, and H. PRITZKOW 1179
- The Crystal Structures of Compounds A_2TeX_6 (A = K, NH_4 , Rb, Cs; X = Cl, Br, I) (In German)
W. ABRIEL and A. DU BOIS 1187
- Trimethyllead-Lithium in Tetrahydrofuran: Synthesis of Trimethyl(trimethylplumbly)silane and of the Trimethylplumblytrihydridoborate Anion (In German)
B. WRACKMEYER and K. HORCHLER 1195
- Electrochemical Investigations of BEDT-TTF (In German)
H. MÜLLER, H. P. FRITZ, A. LERF, and J. O. BESENHARD 1199
- Neutron Diffraction Studies of Li_2CrCl_4 (In German)
P. KUSKE, J. K. COCKCROFT, and H. D. LUTZ 1203
- Cu^{2+} -, Pd^{2+} - and Pt^{2+} -Complexes with $[(\text{en})_2\text{Co}(\text{OH})_2]^+$ Ligands (In German)
U. THEWALT and S. MÜLLER 1206
- Synthesis of New μ -1,4-Diboracyclohexadiene Triple-Decker Complexes (In German)
K.-F. WÖRNER and W. SIEBERT 1211
- Normal Coordinate Analysis of the $^{35}\text{Cl}/^{37}\text{Cl}$ Labelled Fluoro-Chloro-Platinates(IV), $\text{Cs}_2[\text{PtF}_n\text{Cl}_{6-n}]$, $n = 0-6$ (In German)
P. ERLHÖFER and W. PREETZ 1214
- Preparation, Vibration Spectra and Normal Coordinate Analysis of Chloro-Bromo-Rhodates(III) (In German)
W. PREETZ and W. KUHR 1221
- Intermetallic Compounds with HgCl_2 Isoelectronic Anions: Crystal Structure and Vibrational Spectra

- of Na_4HgP_2 , K_4ZnP_2 , K_4CdP_2 and K_4HgP_2
(In German)
B. EISENMANN and M. SOMER 1228
- Structure and Magnetism of Stable Cation Radical Salts: $\text{N,N}'$ -Diethylquinoxalinium Tetraphenylborate as Compared with Pyrazinium and Phenazinium Analogues (In German)
H.-D. HAUSEN, W. KAIM, A. SCHULZ, and E. ROTH 1233
- The System Pyridine-Hydrogen Chloride: Formation and Structure of Crystalline Adducts (In German)
D. MOOTZ and J. HOCKEN 1239
- Hindered Ligand Motions in Transition Metal Complexes. XXXV. Synthesis and Dynamic Behaviour of Dicarbonyl $[\eta^{5:1}$ -(2-cyclopentadienyl)ethyl] $(\eta^2$ -olefin)molybdenum and tungsten (In German)
C. G. KREITER, M. WENZ, and W. MICHELS 1247
- A New Phosphorylation Method *via* O-Diethylboryl Intermediates
W. V. DAHLHOFF and K. M. TABA 1260
- Relationship between the Electronic Structure and Acidic-Basic Properties of 4-Substituted Pyridine N-Oxides
L. CHMURZYŃSKI, A. LIWO, and A. TEMPCZYK 1263
- Synthesis of Hydroxylated Binaphthoquinones *via* Amine/Hydroxyl Exchange – On the Reaction of 2,2'-Binaphthyl-1,4;1',4'-diquinones with Piperidine (In German)
H. LAATSCH 1271
- Diterpenoids from the Root Bark of *Azadirachta indica*
I. ARA, B. S. SIDDIQUI, S. FAIZI, and S. SIDDIQUI 1279
- Thermal Decomposition of Lichen Depsides
S. HUNECK, J. SCHMIDT and R. TABACCHI 1283
- On the 1-Ethyl-2,4,5-triacetylbenzene (In German)
R. RIEMSCHEIDER, G. BUCHLOW, and TH. WONS 1290
- Synthesis of 1,2,3,4,5-Pentaisopropylcyclopentadiene and 1,3,5-Tri-*tert*-butylcyclopentadiene (In German)
H. SITZMANN 1293
- Reactions of 4,4-Bis(trifluoromethyl) Substituted Heterodienes with Alkynes. Part 1: Reactions of 4,4-Bis(trifluoromethyl)-1-oxa-3-azabuta-1,3-dienes with Alkynes (In German)
K. BURGER, N. SEWALD, E. HUBER, and R. OTTLINGER 1298
- Synthesis of Water Soluble Undecagold Clusters for Specific Labelling of Proteins
W. JAHN 1313
- Notes*
- A Platinum(II) Complex with a Phosphine Oxide Adduct of Stannous Chloride
N. DODOFF, N. SPASSOVSKA, and S. VARBANOV 1323
- Crystal Structure of $[\text{MoCl}_2(\text{NSN}) \cdot 2 \text{THF}]_2$; a Metallaheterocycle with the NSN^{4-} Unit (In German)
K. HÖSLER, F. WELLER, and K. DEHNICKE 1325
- Identification of a Baker-type Mechanism in Additions to *p*-Nitrophenyl Isothiocyanate in Diethyl Ether Solution
D. P. N. SATCHELL and R. S. SATCHELL 1329
- A New System of Ionophors Derived from *o,o'*-Biphenyldiol. X-Ray Structure of *o*-Hydroxybiphenyl-*o'*-oxyacetamide
W. O. LIN, J. B. N. DA COSTA, H. G. ALT, and R. D. ROGERS 1331
- The Crystal Structure of $[\text{LFe}]\text{Br}_3 \cdot 4 \text{H}_2\text{O}$ – a Low Spin Hexamineiron(III) Complex (L = 1,2-Bis-(1,4,7-triaza-1-cyclononyl)ethane) (In German)
A. GELENKIRCHEN, K. WIEGHARDT, B. NUBER, and J. WEISS 1333
- Contents of Number 11
- Original Communications*
- Preparation and Spectroscopic Characterization of Primary and Secondary Sulfonium Salts (In German)
R. MINKWITZ, V. GERHARD, and TH. NORKAT 1337

- Preparation of $\text{SCl}_2\text{F}^+\text{MF}_6^-$ ($\text{M} = \text{As}, \text{Sb}$) and a Comprehensive Discussion of the Cations $\text{SCl}_n\text{F}_{3-n}^+$ ($n = 0-3$) (In German)
R. MINKWITZ and G. NOWICKI 1343
- $\text{Li}_7\text{O}_2\text{Br}_3$ – A Further Structure Variant of the New Alkali Metal Chalcogenide Halide Perovskites (In German)
R. WORTMANN, ST. SITTA, and H. SABROWSKY 1348
- Synthesis and Structure of $(\text{MeSe})_3\text{Sb}$ (In German)
H. J. BREUNIG, S. GÜLEÇ, B. KREBS, and M. DARTMANN 1351
- New Evidence of the Interaction of the Vanadyl(IV) Cation with Nucleotides: ^{31}P NMR and IR Measurements in Solution (In German)
S. B. ETCHEVERRY, E. G. FERRER, and E. J. BARAN 1355
- Concerning the System Water–Hydrogen Fluoride: Phase Behaviour and Crystal Structure of $2\text{D}_2\text{O}\cdot 3\text{DF}$, a Deuterated Compound Lacking the Protonated Analogue (In German)
W. POLL, M. LOHMEYER, and D. MOOTZ 1359
- N, N' -Di(*t*-butyl)-*S*-ferrocenylsulfonic Acid Imidoamide – a New Ligand for the Synthesis of Metal Complexes (In German)
H. W. ROESKY, A. GRÜNHAGEN, F. T. EDELMANN, and M. NOLTEMEYER 1365
- Substitution Reactions at the Tetrafluorotantalum Complex $(\eta^5\text{-C}_5\text{Me}_5)\text{-TaF}_4$ (In German)
H. W. ROESKY, F. SCHRUMPF, and M. NOLTEMEYER 1369
- Radiation Induced Br-Transfer from Ethylbromide to Triethylsilane
YU. M. LUGOVOI and N. GETOFF 1373
- Nitrido Complexes of Molybdenum(V); Syntheses, IR, and EPR Spectra. Crystal Structure of $[\text{Na}(15\text{-Crown-5})\text{Na}(\text{THF})]_2[\text{MoNCl}_3\cdot \text{THF}]_4\cdot 2\text{THF}$ (In German)
R. FIGGE, C. FRIEBEL, U. PATT-SIEBEL, U. MÜLLER, and K. DEHNICKE 1377
- Spectroscopic Investigation of the Ion $[\text{FCl}_2\text{V}(\text{}^{15}\text{N}_3\text{S}_2)]^-$; Crystal Structure of $[\text{Na-15-Crown-5}][\text{FCl}_2\text{V}(\text{N}_3\text{S}_2)]$ (In German)
D. REHDER, D. FENSKE, G. BAUM, H. BORGHOLTE, and K. DEHNICKE 1385
- $[\text{Na-15-Crown-5}][\text{ReF}_2\text{Cl}_2(\text{NO})_2]$; Synthesis, IR Spectrum, and Crystal Structure (In German)
ST. VOGLER, K. DEHNICKE, and D. FENSKE 1393
- Preparation and Crystal Structure of $\text{Cs}_4\text{Se}_{16}$ (In German)
W. S. SHELDRIK and H. G. BRAUNBECK 1397
- ^{103}Rh NMR Studies of Chloro-Bromo-Rhodates(III) and Determination of the Stability Constants in the System $[\text{RhCl}_n\text{Br}_{6-n}]^{3-}$, $n = 0-6$ (In German)
W. KUHR, G. PETERS, and W. PREETZ 1402
- Salts of Phosphonic Acid Derivatives: Illustrative Examples of Solid State NMR Spectroscopy
R. K. HARRIS, L. H. MERWIN, and G. HÄGELE 1407
- Metal Complexes of Functional Isocyanides, XVIII. (Alkylideneamino)carbenes by Nucleophilic Addition to Pentacarbonylchromium-coordinated 1,1-Dichloromethyl, 1,1,2-Trichloroethyl and 1-Chlorovinyl Isocyanide (In German)
W. P. FEHLHAMMER and G. BECK 1414
- New Boron-Nitrogen Analogues of Uracil Derivatives
L. KOMOROWSKI and K. NIEDENZU 1421
- Distribution and Valence of the Cations in Spinel Systems with Iron and Vanadium, VIII. Lattice Constants, Mössbauer Spectra and Electronic Properties of the Solid Solution $\text{FeV}_2\text{O}_4\text{-Fe}_3\text{O}_4$ (In German)
E. RIEDEL, J. KÄHLER, and N. PFEIL 1427
- Synthesis and Reactivity of Vinylidene Rhodium Complexes Containing $\text{C}=\text{CHtBu}$ and $\text{C}=\text{CHCO}_2\text{Me}$ as Ligands (In German)
H. WERNER and U. BREKAU 1438
- Outer-Sphere-CT-Interactions between an Organic π -Radical Dication and Main-Group Hexahalogenate Complexes (In German)
R. WEISS and A. M. H. GRIMMEISS 1447

- 9-Aminofluorenum Cations: A New Group of *anti*-Aromatic Molecules
 N. TYUTYULKOV, I. KAVRAKOVA, P. NIKOLOV, and F. DIETZ 1451
- Synthesis and Structure of a New Chiral Oxaziridine from (3-Oxo-camphorsulfonyl)imine
 V. MELADINIS, R. HERRMANN, O. STEIGELMANN, and G. MÜLLER 1453
- Factors Affecting Stability and Equilibria of Free Radicals, XVII. EPR Evidence for Formation of N-Alkoxydicramides on Oxidation of N-Alkoxy-dinitroanilines. Electronic Structure of Aminyl Radicals
 G. STĂNCIUC, M. T. CĂPROIU, H. CĂLDĂRARU, A. CARAGHEORGHEOPOL, T. CONSTANTINESCU, and A. T. BALABAN 1459
- Circular Dichroism Studies of Polyalcohol and Sugar Vanadate(V) Complexes (In German)
 H. BAUER, J. BRUN, A. R. HERNANTO, W. VOELTER, and S. PARASKEWAS 1464
- Notes*
- 5-Deoxybostrycoidin, a New Metabolite Produced by the Fungus *Nectria haematococca* (Berk. and Br.) Wr.
 D. PARISOT, M. DEVYS, and M. BARBIER 1473
- Synthesis of Functionalized Acyclic Nitron Spin Traps
 Y. ZHANG and G. XU 1475
- Contents of Number 12
- Original Communications*
- Na₁₀Ga₆Sn₃, a Compound at the Zintl Border (In German)
 W. BLASE and G. CORDIER 1479
- Synthesis and Crystal Structure of (S₄N₃)₂Se₂Cl₁₀, (S₄N₃)₂Se₂Cl₆, and [(S₄N₃)SeCl₃]_n (In German)
 H. G. STAMMLER and J. WEISS 1483
- Preparation, Spectral Properties and Biological Activity of Cu(II), Zn(II) and Cd(II) Chelates of 8-Hydroxyquinoline-5-sulfonamides
 S. A. IBRAHIM, M. A. EL-GAHAMI, R. M. MAHFOUZ, and K. A. FARGHALI 1488
- Novel Basic Ligands for the Homogenous Catalytic Methanol Carbonylation, XXIV. Rhodium Complexes with (Ether-Phosphane) Ligands of Different Basicity and their Influence on the Methyl Migration (In German)
 E. LINDNER and H. NORZ 1493
- Raman Spectroscopic Discovery of the Hydrogen-thiosulphate Anion, HSSO₃⁻, in Solid NH₄HS₂O₃
 R. STEUDEL and A. PRENZEL 1499
- Gold(I) Complexes of Secondary Phosphines (In German)
 H. SCHMIDBAUR, G. WEIDENHILLER, A. A. M. ALY, O. STEIGELMANN, and G. MÜLLER 1503
- Synthesis and Crystal Structure of PPh₄[ReF₂Cl₂(N₂S₂)] (In German)
 ST. VOGLER, K. DEHNICKE, and W. HILLER 1509
- Cationic Halfsandwich-Type Sulfur Dioxide Complexes of Iron and Ruthenium (In German)
 W. A. SCHENK, U. KARL, and M. R. HORN 1513
- Isolation of Crystalline Potassium Alkanecarbo-selenoates
 H. KAGEYAMA, K. TAKAGI, T. MURAI, and S. KATO 1519
- Syntheses and Crystal Structures of the Crown Ether Complexes (18-Crown-6)·2CH₃CN, [Na-15-Crown-5][ReO₄].CH₃CN, and [Na-15-Crown-5]PF₆ (In German)
 F. WELLER, H. BORGHOLTE, H. STENGER, ST. VOGLER, and K. DEHNICKE 1524
- Compounds of Subvalent Main Group Metal Cations with Dithiolates, Part 4. Crystal Structures of Pb[S(CN)C=C(CN)S] and (AsPh₄)₂{Pb[S(CN)C=C(CN)S]₂} (In German)
 H.-U. HUMMEL and H. MESKE 1531
- P-H Functionalized Zirconocene Phosphido Complexes and the Crystal Structure of a Diazoalkane Insertion Product (In German)
 E. HEY and U. MÜLLER 1538

New Dihydrazido and Oxyamido Derivatives of Phosphoric and Thiophosphoric Acid with Bis(2-chloroethyl)amido Substituents (In German) K. GIERSDORF, U. DIEFENBACH, and U. ENGELHARDT 1545	Photochemical Reactions of Primary Aromatic Amines with Chloromethanes in Solution. II. The Products and Mechanisms of Partial Reactions of Aniline in Tetrachloromethane, Chloroform and Dichloromethane W. BOSZCZYK and T. LATOWSKI 1589
Crystal and Molecular Structure of the Dimeric 1,2-Dioxiphenylene Silicondichloride (In German) W. HÖNLE, U. DETTLAFF-WEGLIKOWSKA, L. WALZ, and H. G. VON SCHNERING 1550	Stereoselective Insertion of Aldehydes and Ketones into the Metal-Carbon Bond of a (η^6 -Fulvene)titanium Complex (In German) G. ERKER and U. KOREK 1593
Influence of Solvent Composition (Water-Dioxane Mixtures) on the Formation Degree of Intramolecular Aromatic-Ring Stacks in Binary Cu(L-Phenylalaninate) ₂ , Cu(L-Tryptophanate) ₂ , and Related Complexes G. LIANG and H. SIGEL 1555	X-Ray Structural Analysis of a Diphosphaadamantane - First Derivative of a Novel Class of Heterocycles (In German) R. NEIDLEIN, A. S. FUNHOFF, and C. KRIEGER 1599
Organometallic Lewis Acids, XLI. μ_2 -CS ₂ - and μ_3 -CS ₂ -Bridged Iron Rhenium Carbonyls (In German) P. M. FRITZ, M. STEIMANN, and W. BECK 1567	<i>Notes</i> First Inter Alkali Metal Tellurides: NaLiTe, KLiTe, KNaTe (In German) R.-D. HITZBLECK, P. VOGT, and H. SABROWSKY 1602
A New Route to Cyclopentadienyl-Substituted Diethylaminocarbyne Complexes of Tungsten (In German) A. C. FILIPPOU and W. GRÜNLEITNER 1572	6-Acetoxy-9-selenabicyclo[3.3.1]-non-2-en: An Unexpected Product of the Se(IV)-Oxidation of 1,5-Cyclooctadien (In German) E. V. DEHMLow and TH. STIEHM 1605
Crystal Structure of SbF ₅ ·SO ₂ (In German) R. MINKWITZ, W. MOLSBECK, and H. PREUT 1581	The Inter Alkali Metal Selenides KLiSe and KNaSe (In German) K. HIPPLER, P. VOGT, R. WORTMANN, and H. SABROWSKY 1607
New Triterpene from <i>Conyza aegyptiaca</i> L. M. A. METWALLY 1584	Buchbesprechung 1610
Photochemical Reactions of Primary Aromatic Amines with Chloromethanes in Solution. I. Spectrochemical Studies W. BOSZCZYK and T. LATOWSKI 1585	Subject Index 1611
	Authors Index 1642

Synthese, Struktur und thermisches Verhalten von Thiophosphorsäuretriamid $\text{SP}(\text{NH}_2)_3$ [1]

Synthesis, Structure, and Thermal Behaviour of Phosphorothionic Triamide $\text{SP}(\text{NH}_2)_3$ [1]

Wolfgang Schnick

Institut für Anorganische Chemie der Universität, Gerhard-Domagk-Straße 1, D-5300 Bonn 1

Z. Naturforsch. **44b**, 942–945 (1989); eingegangen am 23. März 1989

Phosphorothionic Triamide, Synthesis, Structure, Thermal Properties

Phosphorothionic triamide $\text{SP}(\text{NH}_2)_3$ is obtained by slow addition of SPCl_3 dissolved in dry CH_2Cl_2 to a saturated solution of NH_3 in CH_2Cl_2 at -50°C . Ammonium chloride is removed from the resulting precipitate by treatment with HNEt_2 followed by extraction with CH_2Cl_2 . Coarse crystalline $\text{SP}(\text{NH}_2)_3$ is obtained after recrystallization from dry methanol. The crystal structure of $\text{SP}(\text{NH}_2)_3$ has been determined by single crystal X-ray methods (*Pbca*; $a = 922.3(1)$, $b = 953.8(1)$, $c = 1058.4(2)$ pm, $Z = 8$). In the crystals the molecules show non-crystallographic point symmetry C_s . The P–S bond (195.4(1) pm) is slightly longer than in SPCl_3 . From P–N bond lengths of about 166 pm a significant electrostatic strengthening of the P–N single bonds is assumed. Weak intermolecular hydrogen bonding interactions ($\text{N–H}\cdots\text{N} \geq 329.5$ pm; $\text{N–H}\cdots\text{S} \geq 348.3$ pm) are observed.

Investigation of thermal properties shows a melting temperature of 115°C for $\text{SP}(\text{NH}_2)_3$. According to combined DTA/TG and MS investigations above this temperature the compound decomposes by evolution of H_2S and NH_3 to yield amorphous phosphorus(V)nitride.

Einleitung

Stickstoffverbindungen des Phosphors sind in großer Zahl als Phosphazane und Phosphazene in der Literatur beschrieben worden [2, 3]. Demgegenüber liegt nur wenig Information über einfache acyclische Phosphor-Stickstoff-Molekülverbindungen vor. Beispielsweise sind $\text{OP}(\text{NH}_2)_3$ und $\text{H}_3\text{BP}(\text{NH}_2)_3$ dargestellt und strukturell untersucht worden [4, 5]. Beide Verbindungen weisen große Ähnlichkeiten ihrer Molekülgeometrien sowie der relativen Anordnung der Moleküle im Festkörper auf [4].

Bei der systematischen Untersuchung geeigneter Verbindungen, die als Ausgangssubstanz zur Darstellung polymerer Phosphor(V)-nitride in Frage kommen, stießen wir auf Thiophosphorsäuretriamid $\text{SP}(\text{NH}_2)_3$, das nun erstmals in reiner Form dargestellt und strukturell durch Röntgenstrukturanalyse an Einkristallen charakterisiert wurde. Im Hinblick auf die Verwendung als Precursor-Verbindung zur pyrolytischen Darstellung von polymerem Phosphor(V)-nitrid ist außerdem das thermische Verhalten dieser Verbindung untersucht worden.

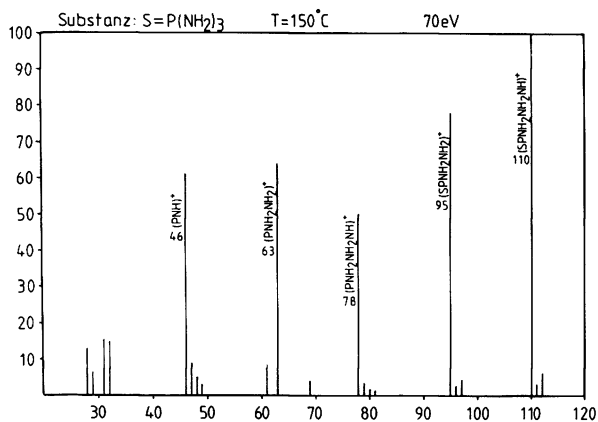
Experimenteller Teil

Synthese von Thiophosphorsäuretriamid

Die Darstellung erfolgte in Anlehnung an eine von R. Klement *et al.* mitgeteilte Vorschrift [6, 7]. Unter Feuchtigkeitsausschluß (Argon-Atmosphäre) wurden 700 ml trockenes und frisch destilliertes Dichlormethan bei -50°C mit Ammoniak gesättigt. Unter starkem Rühren wurde tropfenweise eine ebenfalls gekühlte Lösung von 16 ml PSCl_3 (0,1 mol) in 45 ml Dichlormethan zugegeben und die Ammoniakleitung noch eine weitere Stunde fortgesetzt. Nach langsamer Erwärmung auf Raumtemperatur wurde der entstandene Niederschlag abfiltriert und durch mehrfaches Kochen mit einer Lösung von 60 ml Diethylamin in 100 ml Dichlormethan von Ammoniumchlorid befreit. Der Feststoff wurde schließlich mit Dichlormethan gewaschen, bis keine Chlorid-Ionen im Filtrat mehr nachzuweisen waren. Reines, grobkristallines $\text{SP}(\text{NH}_2)_3$ wurde durch Kristallisation aus trockenem Methanol erhalten.

Thermisches Verhalten von Thiophosphorsäuretriamid

Zur Untersuchung des thermischen Verhaltens von $\text{SP}(\text{NH}_2)_3$ wurden kombinierte DTA/TG-Messungen mit unterschiedlichen Aufheizraten (0,5–5 K/min) im Temperaturbereich zwischen 25 und 900°C durchgeführt. Die Schmelztemperatur wurde dabei durch Extrapolation auf eine Aufheizrate von 0 K/min bestimmt. Oberhalb des Schmelz-

Abb. 1. Massenspektrum von $SP(NH_2)_3$, $T = 150^\circ$.

punktes durchgeführte massenspektroskopische Untersuchungen (vgl. Abb. 1) dienten zur Aufklärung der thermischen Zersetzung und Identifizierung der auftretenden gasförmigen Produkte. Die in Abb. 1 den beobachteten Massenpeaks zugeordneten Fragmentstöchiometrien wurden unter Berücksichtigung der natürlichen Isotopenverteilung der beteiligten Elemente erhalten.

Strukturbestimmung und Kristalldaten von $SP(NH_2)_3$

Für die Strukturbestimmung (Tab. I) wurde ein Einkristall der ungefähren Größe $0,2 \times 0,1 \times 0,1$ mm

Tab. I. Kristalldaten und Parameter der Strukturbestimmung von $SP(NH_2)_3$.

Formel	$SP(NH_2)_3$
Molmasse	111,0
Gitterkonstanten	$a = 922,3(1)$ pm $b = 953,8(1)$ pm $c = 1058,4(2)$ pm
Zellvolumen	$V = 931,0 \cdot 10^6$ pm ³
Formeleinheiten	$Z = 8$
Berechnete Dichte	$\rho = 1,58$ g · cm ⁻³
Kristallsystem	orthorhombisch
Raumgruppe	$Pbca$
Strahlung	Mo-K α
Meßtemperatur	21 °C
Meßmethode	ω -2 θ -Scan
Beugungswinkelbereich	$3^\circ \leq 2\theta \leq 50^\circ$
Kristallgröße in mm	$0,2 \times 0,1 \times 0,1$
Anzahl der beobachteten Reflexe	9738
Anzahl der unabh. Reflexe	678
mit $I_o \geq 3 \cdot \sigma(I_o)$	
Verfeinerte Parameter	70
Linearer Absorptionskoeffizient	$\mu = 7,84$ cm ⁻¹
R-Werte	$R = 0,066$ $R_w = 0,030$ $w = 5,1/\sigma^2(F_o)$

verwendet. Die Raumgruppe der Verbindung ($Pbca$, Nr. 61) wurde auf der Basis von Präzessionsaufnahmen bestimmt. Zur Ermittlung genauer Gitterkonstanten wurden Pulverdiffraktometermessungen [8] herangezogen, die in Übereinstimmung mit den Einkristalldaten vollständig indiziert wurden (30 beobachtete Pulverreflexe im Bereich $15^\circ \leq 2\theta \leq 73^\circ$). Die Orientierung des Einkristalls auf dem Vierkreisdiffraktometer [9] wurde auf der Basis von 25 gleichmäßig im reziproken Raum verteilten Reflexen bestimmt. Zur Strukturanalyse wurden 9738 Reflexe vermessen, von denen 4048 eine Intensität $I \geq 2\sigma(I)$ besaßen. Nach Mittelung in der Laue-Klasse mmm ($R_{int} = 0,031$) wurden 678 symmetrieunabhängige Intensitätswerte erhalten.

Die Lagen der P-, S- und N-Atome wurden durch Direkte Methoden mit dem Programm SHELX-76 [10] lokalisiert. Nach Verfeinerung ihrer Koordinaten konnten die Positionen aller sechs Wasserstoffatome des Moleküls aus einer Differenzfouriersynthese eindeutig bestimmt werden. Die endgültige Verfeinerung der Atomparameter unter Einführung anisotroper Temperaturparameter (H-Atome isotrop) ergab $R = 0,066$ bzw. $R_w = 0,03$ mit $w = 5,08/\sigma^2(F_o)$.

Die mit Röntgenbeugungsmethoden ermittelten Atomlagen stellen lokale Maxima der Elektronendichteverteilung im Kristall dar, die insbesondere im Fall extrem leichter Atome wie Wasserstoff bekannterweise nicht mit den tatsächlichen Atompositionen exakt übereinstimmen müssen. Dieser Sachverhalt kommt in zu kurzen verfeinerten N–H-Bindungslängen (gefundene Werte: zwischen 75 und 95 pm) zum Ausdruck, für die ein Wert von etwa 100 pm erwartet werden kann [11]. Aus diesem Grund wurden idealisierte Wasserstoffpositionen (N–H-Bindungslängen: 100 pm) in Anlehnung an die Konformatio-

Tab. II. Ortsparameter und isotrope äquivalente Temperaturparameter U_{eq} der Atome in $SP(NH_2)_3$. $U_{eq} = 1/3(U_{11} + U_{22} + U_{33})$. U ist in Einheiten von [pm²] angegeben. Standardabweichungen in Klammern.

Atom	x	y	z	U
S	0,1570(1)	0,4483(1)	0,0665(1)	376(6)
P	0,3370(1)	0,4095(1)	0,1574(1)	255(5)
N1	0,4234(3)	0,5594(3)	0,1825(3)	359(20)
N2	0,4682(3)	0,3148(3)	0,0916(3)	335(19)
N3	0,3017(3)	0,3121(3)	0,2833(3)	384(19)
H1a	0,5084(3)	0,5422(3)	0,2391(3)	781(67)
H1b	0,3564(3)	0,6282(3)	0,2233(3)	781(67)
H2a	0,5012(3)	0,3625(3)	0,0125(3)	781(67)
H2b	0,4310(3)	0,2191(3)	0,0707(3)	781(67)
H3a	0,3908(3)	0,3042(3)	0,3366(3)	781(67)
H3b	0,2224(3)	0,3570(3)	0,3335(3)	781(67)

nen der verfeinerten H-Positionen berechnet und für die Strukturdiskussion zugrunde gelegt. Die isotropen Temperaturfaktoren der Wasserstoffatome wurden dabei gemeinsam verfeinert (Tab. II) [12].

Ergebnisse und Diskussion

Eigenschaften und thermisches Verhalten von Thiophosphorsäuretriamid

Thiophosphorsäuretriamid bildet farblose Kristalle, die sich an der Luft im Verlauf von mehreren Wochen unter Hydrolyse zersetzen [6]. Unter Argon-Schutzgas kann die Substanz jedoch unzersetzt aufbewahrt werden. Thiophosphorsäuretriamid besitzt einen Schmelzpunkt von 115 °C. Bereits kurz oberhalb dieser Temperatur beginnt die thermische Zersetzung der Substanz unter endothermer Abspaltung von H₂S und NH₃, die schließlich bei Temperaturen oberhalb von 850 °C zur Bildung von polymerem Phosphor(V)-nitrid führt, welches unter den gegebenen Bedingungen in amorpher Form anfällt.

Diskussion der Struktur von SP(NH₂)₃

Im Kristall wird ein kristallographisch unabhängiges Molekül SP(NH₂)₃ gefunden.

Für die freie Spezies SP(NH₂)₃ könnte C_{3v}-Symmetrie erwartet werden [13]. Unter Berücksichtigung der experimentell bestimmten Konformationen der NH₂-Gruppen (Abb. 2) sowie der bemerkenswerten Aufweitung des Bindungswinkels S–P–N₂ auf 121° (vgl. Tab. III) ergibt sich jedoch im Festkörper für das Molekül die nicht-kristallographische Punktsymmetrie C_s mit einer Spiegelebene durch die Atome P, S und N₂. Die Bindungswinkel S–P–N₁ und S–P–N₃ entsprechen mit 108,9 bzw. 109,6° annähernd einem idealen Tetraederwinkel.

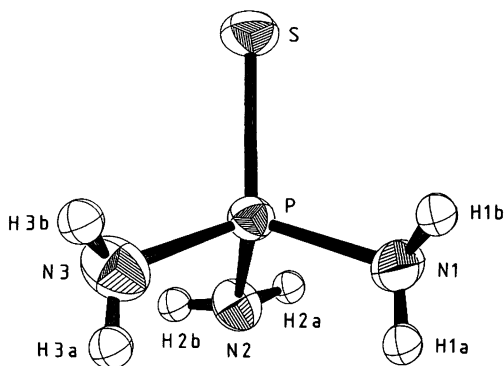


Abb. 2. Molekülstruktur von SP(NH₂)₃ im Kristall.

Tab. III. Interatomare Abstände und Winkel in SP(NH₂)₃.

Bindungsabstände [pm] und Winkel [°]			
P–N ₃	165,7(3)	N ₃ –P–N ₂	100,1(2)
P–N ₁	165,8(3)	N ₂ –P–N ₁	100,7(2)
P–N ₂	166,2(3)	N ₁ –P–S	108,9(1)
P–S	195,4(1)	N ₃ –P–S	109,6(1)
		N ₃ –P–N ₁	116,7(2)
		N ₂ –P–S	121,0(1)
Kürzeste intermolekulare N⋯H–N- und S⋯H–N-Abstände [pm] sowie Winkel an den Wasserstoffatomen [°] (in Klammern)			
N ₁ ⋯H _{2a} –N ₂	329,5		(171,8)
N ₂ ⋯H _{3b} –N ₃	334,9		(141,5)
N ₃ ⋯H _{1b} –N ₁	335,5		(169,4)
S⋯H _{2b} –N ₂	348,3		(167,7)
S⋯H _{1a} –N ₁	358,1		(158,9)

Der Phosphor–Schwefel-Bindungsabstand ist mit 195,4(1) pm um etwa 6 pm länger als der entsprechende Wert in SPCl₃ [14], was auf eine leichte Schwächung dieser Bindung zurückgeführt wird. Die drei Phosphor–Stickstoff-Bindungen besitzen eine mittlere Länge von 165,9 pm. Verglichen mit dem für eine P–N-Einfachbindung zu erwartenden Wert von 177 pm [15], führen offensichtlich elektrostatische Wechselwirkungen zu einer signifikanten Bindungsverstärkung. Neben den oben erwähnten Winkeln S–P–N₁ und S–P–N₃ entsprechen auch die H–N–H-Bindungswinkel auf der Basis der ursprünglich verfeinerten und lokalisierten H-Atompositionen im Mittel annähernd Tetraederwinkeln von 109° (H_{1a}–N₁–H_{1b}: 109°; H_{2a}–N₂–H_{2b}: 112°; H_{3a}–N₃–H_{3b}: 105°). Die kürzesten intermolekularen Kontaktabstände lassen schwache Wasserstoffbrückenbindungen vermuten (N–H⋯N ab 330 pm; N–H⋯S ab 348 pm; vgl. Tab. III). Offensichtlich nehmen jedoch nur 5 Wasserstoffatome an solchen Brückenbindungen teil, während das sechste Proton (H_{3a}) einen signifikant längeren intermolekularen Abstand zum nächsten Heteroatom ausbildet (N₃–H_{3a}⋯N₃: 352 pm, Winkel an H₃: 120,5°). Bei der ursprünglichen Verfeinerung der H-Positionen ergab sich genau für dieses Wasserstoffatom mit 76 pm signifikant der kürzeste NH-Abstand (die verfeinerten N–H-Bindungsabstände lagen zwischen 76 pm (H_{3a}) und 95 pm (H_{2a})).

Geringfügige Abweichungen der einzelnen Atompositionen von der C_s-Symmetrie des Moleküls werden auf Unterschiede im Wasserstoffbrückenbindungssystem der Verbindung zurückgeführt.

Die in Abb. 2 dargestellten Konformationen der NH_2 -Gruppen sowie die bemerkenswerte Aufweitung des $\text{X}-\text{P}-\text{N}_2$ -Winkels werden in analoger Weise in den Verbindungen $\text{XP}(\text{NH}_2)_3$ ($\text{X} = \text{O}$ [4], BH_3 [5]) gefunden. Beide Verbindungen besitzen trotz unterschiedlicher Substituenten X am Phosphoratom und daraus resultierender Unterschiede in ihren Wasserstoffbrückenbindungssystemen vergleichbare Molekülanordnungen im Festkörper, was sich bereits in der Ähnlichkeit der Gittermetrik andeutet ($\text{OP}(\text{NH}_2)_3$: $\text{P}2_1/c$; $Z = 4$; $a = 840$, $b = 877$, $c = 542$ pm; $\beta = 94,5^\circ$ bzw. $\text{BH}_3\text{P}(\text{NH}_2)_3$: $\text{P}2_1/c$; $Z = 4$; $a = 941$, $b = 949$, $c = 623$ pm $\beta = 100,3^\circ$). Im Fall von $\text{SP}(\text{NH}_2)_3$ tritt dagegen eine deutlich abweichende Anordnung der Moleküle im Festkörper auf, die zu orthorhombischer Kristallsymmetrie führt. Im Falle von $\text{SP}(\text{NH}_2)_3$ werden deutlich schwächere

Wasserstoffbrückenbindungen als in $\text{OP}(\text{NH}_2)_3$ und $\text{BH}_3\text{P}(\text{NH}_2)_3$ beobachtet. Die bei allen drei Verbindungen in analoger Weise auftretenden Konformationen der NH_2 -Gruppen sowie die bemerkenswerte Aufweitung des $\text{X}-\text{P}-\text{N}_2$ -Bindungswinkels auf etwa 120° scheinen deshalb nicht allein durch Packungseffekte im Festkörper bzw. durch Einflüsse von Wasserstoffbrückenbindungen erklärbar zu sein. Auch abstoßende Wechselwirkungen zwischen dem Substituenten X am Phosphoratom und dem *lone pair* des Stickstoffatoms N_2 können aufgrund der beobachteten *trans*-Stellung zwischen beiden als Ursache für die Aufweitung des $\text{X}-\text{P}-\text{N}_2$ -Winkels ausgeschlossen werden.

Herrn Prof. Dr. Martin Jansen danke ich für die Unterstützung mit Sachmitteln.

-
- [1] Vgl. Tagungsabstract, 28. Diskussionstagung der AGKr, Hannover, 1.-3. 1989; W. Schnick, Z. Kristallogr. **186**, 268 (1989).
- [2] H. R. Allcock, Chem. Rev. **72**, 315 (1972).
- [3] H. R. Allcock, „Phosphorus Nitrogen Compounds“, Academic Press, New York (1972).
- [4] G. J. Bullen, F. S. Stephens und R. J. Wade, J. Chem. Soc. **A** **1969**, 1804.
- [5] C. E. Nordman, Acta Crystallogr. **13**, 535 (1960).
- [6] R. Klement und O. Koch, Chem. Ber. **87**, 333 (1954).
- [7] R. Klement, Inorg. Synth. **6**, 111 (1960).
- [8] Automatisches Pulverdiffraktometersystem STADIP, Fa. Stoe, Darmstadt.
- [9] Automatisches Einkristalldiffraktometer CAD4, Fa. Enraf-Nonius, Delft.
- [10] G. M. Sheldrick, SHELX-76, „Program for Crystal Structure Determination“, Cambridge (1976).
- [11] A. F. Wells, „Structural Inorganic Chemistry“, Clarendon Press, Oxford (1984).
- [12] Weitere Einzelheiten zur Kristallstrukturbestimmung können beim Fachinformationszentrum Karlsruhe, D-7514 Eggenstein-Leopoldshafen 2, unter Angabe der Hinterlegungsnummer CSD 53763, des Autors und des Zeitschriftenzitates angefordert werden.
- [13] R. Dorschner, F. Choplin und G. Kaufmann, J. Mol. Struct. **22**, 421 (1974).
- [14] T. Moritani, K. Kochitsu und Y. Morino, Inorg. Chem. **10**, 344 (1971).
- [15] D. E. C. Corbridge, „The Structural Chemistry of Phosphorus“, S. 7, Elsevier, New York (1974).