Synthesis and X-ray Molecular Structure of $(PNP)_2[Mo^{IV}(C_6H_4S_2-1,2)_3]$ Completing the Structural Characterization of the Series $[Mo(C_6H_4S_2-1,2)_3]^{n-1}$ (n = 0, 1, 2)

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The tris(benzene-1,2-dithiolato) complex (Li)₂[Mo^{IV}(C₆H₄S₂-1,2)₃] {(Li)₂[Mo^{IV}(bdt)₃]} (bdt²⁻ = C₆H₄S₂-1,2 dianion) was synthesized from [MoCl₄(CH₃CN)₂], (H₂bdt), and *n*BuLi in THF. Complex (Li)₂[Mo^{IV}(bdt)₃] undergoes aerial oxidation to give Li[Mo^V(bdt)₃]. Both complexes were crystallized from methanol as the salts (PNP)₂[Mo^{IV}(bdt)₃] and (PNP)[Mo^{V-}(bdt)₃] {PNP⁺ = bis(triphenylphosphoranylidene)ammonium cation}, and their molecular structures were determined by

X-ray diffraction. The molybdenum(IV) complex $[Mo^{IV}-(bdt)_3]^{2-}$ assumes a distorted trigonal prismatic coordination geometry (average twist angle $\phi=24.8^\circ$) while the coordination geometry of $[Mo^V(bdt)_3]^-$ is best described as distorted octahedral (average twist angle $\phi=34.1^\circ$).

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Introduction

The first trigonal prismatic (TP) tris(dithiolene) metal complex, tris(cis-1,2-diphenylethylene-1,2-dithiolato)rhenium, was reported in 1965.^[1] Ever since, the reasons for the formation of complexes with trigonal prismatic coordination geometry over octahedral complexes has been a subject for discussion.^[2] Early explanations based on molecular orbital schemes indicated that metal centers with a formal d⁰ electron configuration preferentially form trigonal prismatic tris(dithiolene) transition metal complexes. In the series of tris(benzene-1,2-dithiolato) complexes, [W^{VI}(bdt)₃] is trigonal prismatic (twist angle $\varphi = 0^{\circ}$),^[3] while the geometry of $[W^{V}(bdt)_{3}]^{-}$ was found to be closer to octahedral (average twist angle $\varphi = 33^{\circ}$) than to trigonal prismatic.^[4] Surprisingly, the $[W^{IV}(bdt)_3]^{2-}$ complex exhibits a geometry close to perfect trigonal prismatic (average twist angle φ = 3.5°).^[5] In the homologous series of molybdenum complexes [Mo^V(bdt)₃]⁻ assumes a geometry analogous to the W^V complex, between octahedral and trigonal prismatic (average twist angle $\varphi = 33.5^{\circ}$),^[6] while the complex [Mo^{VI}-(bdt)₃] is, as expected, trigonal prismatic (average twist angle $\varphi = 0^{\circ}$).^[7] The molecular structure of $[Mo^{IV}(bdt)_3]^{2-}$ has not been reported. The pseudooctahedral geometry of the d^0 complex $[Zr^{IV}(bdt)_3]^{2-}$ is rather unexpected^[8] when compared to the trigonal prismatic^[9] d^0 complex [Nb^V(bdt)₃]⁻. It appears that the stepwise reduction of the *formal* d⁰ center in $[M^{VI}(bdt)_3]$ (M = Mo, W) complexes does not gen-

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erally enhance the tendency for the formation of octahedral complexes, and that the geometry of a particular complex is not governed only by electronic factors. Ligand constraints,^[10] matching of ligand and metal d orbital energies, symmetry of ligand π orbitals, inter-donor interactions, and the overall charge of the complex have been suggested to be additional important factors.^[11]

The situation is further complicated by the non-innocent nature of the bdt^{2–} ligand. Wieghardt has shown that an intramolecular redox reaction can convert coordinated bdt^{2–} into a coordinated *o*-dithiobenzosemiquinonate(1–) radical anion by the reduction of the metal center. Under such conditions, the *spectroscopic* oxidation state of the metal differs from the formal oxidation state. The geometrical changes within the ligand that are associated with the intramolecular redox reaction have been outlined for square planar bdt^{2–} complexes.^[12]

As part of our ongoing effort to shed light on the relationship between the *formal* oxidation state of the metal and the molecular structure of $[M(bdt)_3]^{n-}$ (M = Mo, W) complexes, we present here the preparation and molecular structure of the yet unknown derivative $(PNP)_2[Mo^{IV}-(bdt)_3]^{2-}$. In addition, the previously described^[6] complex anion $[Mo^V(bdt)_3]^-$ was prepared again, and the crystal structure of the salt $(PNP)[Mo^V(bdt)_3]$ was elucidated and compared to the molecular structure reported for (nBu_4N) - $[Mo^V(bdt)_3]$.^[6a]

Results and Discussion

Transition metal tris(benzene-1,2-dithiolato) complexes have been synthesized by the reaction of the hexahalides

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 MX_6 with an excess of benzene-1,2-dithiol (H₂bdt) in CCl₄, a reaction that liberates gaseous HCl.^[2d] Later Sellmann et al. showed that benzene-1,2-dithiol that is deprotonated with *n*BuLi (Li₂bdt) reacts with [MoCl₄(THF)₂] to give (Li)₂[Mo^{IV}(bdt)₃], while the reaction of benzene-1,2-dithiol with [MoCl₄(THF)₂] gives [Mo^{VI}(bdt)₃].^[6b] Complex [Mo^{VI}(bdt)₃] can be reduced to the complexes [Mo^{V-} (bdt)₃]⁻ and [Mo^{IV}(bdt)₃]²-with *n*BuLi.

We prepared (Li)₂[Mo^{IV}(bdt)₃] by the deprotonation of H₂bdt with *n*BuLi at -78 °C in THF followed by the the dropwise addition of a DMF solution of [MoCl₄(CH₃CN)₂] at -78 °C (Scheme 1). Below -40 °C the reaction mixture remained unchanged and colorless. Warming to above -40 °C led to a color change in the reaction mixture to deep blue, which is typical for solutions containing the [Mo^{IV}(bdt)₃]²⁻ anion.^[6b] The solution was warmed to room temperature, stirred at this temperature overnight, and then heated under reflux for 1 h. Standard workup procedures gave (Li)₂[Mo^{IV}(bdt)₃] in 76% yield. Blue, air-sensitive crystals of (PNP)₂[Mo^{IV}(bdt)₃]·6 MeOH suitable for X-ray analysis were obtained by addition of a methanolic solution of PNPCl to a methanolic solution of (Li)₂[Mo^{IV}(bdt)₃]. Aerial oxidation of (Li)₂[Mo^{IV}(bdt)₃] in methanol gave a green solution of (Li)[Mo^V(bdt)₃]. Addition of a methanolic solution of PNPC1 yielded green, air-stable crystals of (PNP)[Mo^V(bdt)₃] (Scheme 1).



Scheme 1. Preparation of (Li)₂[Mo^{IV}(bdt)₃] and (Li)[Mo^V(bdt)₃].

The ¹H NMR spectrum of complex (Li)₂[Mo^{IV}(bdt)₃] exhibits two multiplets at δ = 7.37 ppm and δ = 6.57 ppm for the benzene protons, and the coupling pattern corresponds to a symmetrical AA'XX' spin system (Figure 1). Two resonances for the benzene carbon atoms were observed in the ¹³C NMR spectrum at δ = 119.8 ppm and δ = 126.5 ppm in addition to the signal for the *ipso*-carbon atom at δ = 155.1 ppm. The difference in the line widths of these signals appears to be an artifact of the data acquisition method.



Figure 1. ¹³C NMR (top) and ¹H NMR spectra (bottom) of (Li)₂[Mo^{IV}(bdt)₃] (* = solvent).



Figure 2. Left: molecular structure of the $[Mo^{IV}(bdt)_3]^{2-}$ anion with the crystallographic numbering scheme. Hydrogen atoms have been omitted. The anion resides on a twofold axis which bisects the C9–C9* bond (symmetry code *: 1 - x, y, 1/2 - z). Selected bond lengths [Å] and angles [°]: Mo–S1 2.3952(14), Mo–S2 2.3981(12), Mo–S3 2.3940(12), S1–C1 1.765(3), S2–C2 1.761(3), S3–C7 1.750(4); S1–Mo–S2 81.06(4), S1–Mo–S3 115.68(4), S1–Mo–S1* 152.33(5), S1–Mo–S2* 84.93(5), S1–Mo–S3* 85.96(4), S2–Mo–S3 83.22(5), S2–Mo–S1* 84.93(5), S2–Mo–S2* 118.70(5), S2–Mo–S3* 153.06(3), S3–Mo–S3* 81.31(6). Right: drawing of the MoS₆ core showing the twist angle φ between the S₃ planes.

The ¹H NMR resonances correspond well to the values reported for $(NEt_4)_2[W(bdt)_3]$.^[5] The molecular structure of $(PNP)_2[Mo(bdt)_3]$ ·6 MeOH was determined by X-ray diffraction (Figure 2).

The overall solid state molecular structure of the complex anion [Mo^{IV}(bdt)₃]²⁻ differs from that of the heavier homologue $[W^{IV}(bdt)_3]^{2-}$. The molybdenum(IV) ion in $[Mo(bdt)_3]^{2-}$ is coordinated by six sulfur atoms from three bdt²⁻ ligands in a strongly distorted trigonal prismatic fashion. The average twist angle $\varphi^{[13]}$ (see Figure 2, right) is 24.8° for $[Mo(bdt)_3]^{2-}$ compared to $\varphi = 3.5^{\circ}$ for [W-(bdt)₃]^{2-.[5]} The three different twist angles observed for $[Mo(bdt)_3]^{2-}$ result from the noncoplanar arrangement of the two S₃ planes. The bending of the S–C–C–S plane away from the S-Mo-S-plane is small in [Mo^{IV}(bdt)₃]²⁻ (about 0.8°) while large bending angles were observed for- $[Mo^{VI}(bdt)_3]$ (13.1, 21.1, 30.0°)^[7] and $[W^{VI}(bdt)_3]$ (13.5, 22.6, 32.1°).^[3] On the basis of Fenske-Hall MO calculations it has been suggested that the bending of the ligand can be viewed as a second-order Jahn-Teller distortion, which is most favored for d⁰ metal centers in a trigonal prismatic coordination environment.^[14] While the electronic factors provide the principal driving force, the bulk of the dithiolate ligand also plays a role in determining the molecular structures. This becomes obvious when the three different bending angles for $[M^{VI}(bdt)_3]$ (M = Mo, W) complexes are considered.

For a comparison of the bond parameters in $[Mo^{IV}-(bdt)]^{2-}$ and $[Mo^{V}(bdt)]^{-}$, which have been obtained under similar conditions (153–173 K) and with identical counterions, we determined the molecular structure of (PNP)[Mo^V(bdt)₃] (Figure 3). The molecular structure of $(nBu_4N)[Mo^{V}(bdt)_3]$ has been determined previously at room temperature.^[6a]



Figure 3. Molecular structure of $[Mo^V(bdt)_3]^-$ with the crystallographic numbering scheme. Hydrogen atoms have been omitted. Selected bonds lengths [Å] and angles [°]: Mo–S1 2.3880(8), Mo–S2 2.4020(8), Mo–S3 2.3702(7), Mo–S4 2.3778(8), Mo–S5 2.3999(8), Mo–S6 2.3785(7); S1–Mo–S2 81.81(3), S1–Mo–S3 95.42(3), S1–Mo–S4 160.05(3), S1–Mo–S5 82.89(3), S1–Mo–S6 102.93(3), S2–Mo–S3 107.72(3), S2–Mo–S4 79.91(3), S2–Mo–S5 162.41(3), S2–Mo–S6 92.28(2), S3–Mo–S4 82.64(3), S3–Mo–S5 82.31(3), S3–Mo–S6 154.62(3), S4–Mo–S5 116.31(3), S4–Mo–S6 85.78(3), S5–Mo–S6 82.73(2).

In both the PNP⁺ and the nBu_4N^+ salts, the structure of the anion $[Mo(bdt)_3]^-$ is an unsymmetrical polyhedron, exhibiting a geometry between trigonal prismatic and octahedral (average twist angle $\varphi = 34.1^{\circ}$ for the PNP⁺ salt and $\varphi = 33.5^{\circ}$ for the *n*Bu₄N⁺ salt). However, the [Mo^V(bdt)₃]⁻ anions in the two salts show a considerable difference regarding the orientation of the S₃ planes that define the twist angle φ (Figure 2). While the anion in the *n*Bu₄N⁺ salt exhibits three rather similar angles (30.4, 34.4, 35.6°), which indicates an almost coplanar arrangement of the S₃ planes, three significantly different values were observed for (PNP)[Mo(bdt)₃] (18.4, 36.3, 47.8°). The S1/S3/S5 plane in this complex is tilted by 7.2° with respect to the S2/S4/S6 plane. Crystal packing effects might be responsible for this observation, which again illustrates that electronic effects are not solely responsible for the molecular structure of $[M(bdt)_3]^{n-}$ complexes.

The "innocent" and "non-innocent" nature of ligands like bdt²⁻ has recently been discussed intensively.^[12] For O,O'-coordinated catecholates or o-benzosemiquinonate-(1-)- π -radicals a number of typical structural and spectroscopic features have been described, which allow the detection and identification of such ligands in coordination compounds.^[15] The picture was not so clear for the corresponding o-dithio derivatives like bdt²⁻. Recently square-planar complexes of the type $[M(bdt)_2]^{n-}$ (M = Au^{III}, Ni^{II})^[12] have been described, and structural parameters associated with dithiolato(2-) and o-dithiobenzosemiquinonato(1-) coordination have been worked out. This allows, in principle, the assignment of the oxidation level of a benzene-1,2-dithiolato ligand in a complex. For complexes of the type [M- $(bdt)_2$ ^{*n*-} this assignment becomes complicated if a benzene-1,2-dithiolate and an o-dithiobenzosemiquinonate ligand are coordinated at the same time, as the structural differences between the two ligand types are small. Statistical disorder problems may hamper the identification of the different oxidation levels of the ligand and this becomes even more complicated for complexes of the type $[M(bdt)_3]^{n-1}$ with three bdt²⁻ ligands, each of which can undergo intramolecular oxidation.

We have studied the structural parameters in the series $[Mo(bdt)_3]^{n-}$ (n = 0, 1, 2, Figure 4) and found some trends in the Mo–S, S–C and C–C bond lengths. On the basis of the geometric parameters of the *o*-dithiolato ligands in $[Mo^{VI}(bdt)_3]$ and the paramagnetism observed for the complex, Bennet et al.^[7] proposed, as early as 1976, the presence of a dithioketonic ligand species in $[Mo^{VI}(bdt)_3]$. On the basis of Wieghardt's investigations,^[12] we believe that the ligand in $[Mo^{VI}(bdt)_3]$ is best described as an *o*-dithiobenzosemiquinonate(1–) radical anion.

In the series of $[Mo(bdt)_3]^{n-}$ complexes, the C–S bond lengths increase as the metal oxidation state changes from Mo^{VI} to Mo^{IV} (Figure 4). Mo^{VI} is capable of oxidizing the *o*-dithiolato ligand to a higher degree than Mo^{IV} , leading to a thioketonic ligand which is detectable by the decrease in the C–S bond lengths. This postulate is corroborated by an evaluation of the C–C bond lengths within the aromatic ring. In summary, the trends in the structural parameters



Figure 4. Average bond lengths [Å] for complexe anions of the type $[Mo(bdt)_3]^{n-}$ (n = 2, 1, 0) including literature data for $[Mo^{VI}-(bdt)_3]^{[7]}$

indicate that the bdt^{2-} ligand is at least partially oxidized upon coordination to transition metals in high oxidation states (Mo^{VI}).

From the variation of the twist angle φ in the series $[Mo(bdt)_3]^{n-}$ (n = 0, 1, 2) it appears that the *formal* d electron configuration is not the only governing principle for the formation of certain coordination polyhedra. These results indicate once more that the stabilization of a trigonal prismatic coordination geometry does not only depend on the electronic situation at the central metal atom, but instead must be considered a complicated process involving various factors, including the counterions that are present.

Experimental Section

General Remarks: Unless stated otherwise, all manipulations were carried out under dry argon by means of standard Schlenk techniques. THF was freshly distilled from Na/benzophenone prior to use. Methanol was dried over magnesium and freshly distilled. The DMF purchased contained molecular sieves and was used as received. [MoCl₄(CH₃CN)₂] was purchased from Aldrich.

(Li)₂[Mo^{IV}(bdt)₃]: A sample of benzene-1,2-dithiol (423 mg, 3.0 mmol) was dissolved in THF (20 mL). The solution was cooled to -78 °C and *n*BuLi (6.0 mmol, 2.4 mL of a 2.5 M solution in hexane) was added dropwise. [MoCl₄(CH₃CN)₂] (320 mg, 1 mmol) in DMF (5 mL) was then added, and the reaction mixture was allowed to warm slowly to ambient temperature. While warming, the color of the solution turned deep blue. The reaction mixture was stirred overnight and then heated under reflux for 1 h. Thereafter all solvents were removed and the crude reaction product was washed with diethyl ether and dried in vacuo. Yield: 403 mg (0.76 mmol, 76%). C₁₈H₁₂Li₂MoS₆ (530.48): calcd. C 40.76, H 2.28; found C 41.43, H 2.40. ¹H NMR (200 MHz, [D₇]DMF): $\delta =$ 7.37 (dd, ³J = 8.8, ⁴J = 2.4 Hz, 6 H, Ar–H), 6.57 (dd, ³J = 8.8, ⁴J

= 2.4 Hz, 6 H, Ar–H). ¹³C NMR (50 MHz, [D₇]DMF): δ = 155.1 (*ipso*-C), 126.5 (Ar–C), 119.8 (Ar–C).

 $\begin{array}{l} (PNP)_2[Mo^{IV}(bdt)_3]\cdot 6\,MeOH: \mbox{ Slow diffusion of a methanolic solution of PNPCl (PNPCl = bis(triphenylphosphoranylidene)ammonium chloride) into a solution of (Li)_2[Mo^{IV}(bdt)_3] in methanol led to the precipitation of deep blue, air-sensitive single crystals of (PNP)_2[Mo^{IV}(bdt)_3]\cdot 6\,MeOH$ which were suitable for an X-ray diffraction study. These crystals were characterized by X-ray diffraction only.

(PNP)[Mo^V(bdt)₃]: Complex $(Li)_2[Mo^{IV}(bdt)_3]$ dissolved in methanol was oxidized by exposure to air. A green solution of Li-[Mo^V(bdt)₃] resulted. Green crystals of (PNP)[Mo^V(bdt)₃] were obtained by the slow addition of a methanolic solution of PNPCl.

X-ray Crystallographic Study of (PNP)2[Mo^{IV}(bdt)3]·6MeOH: A suitable crystal $(0.20 \times 0.10 \times 0.07 \text{ mm}^3)$ was mounted on a Bruker AXS APEX diffractometer equipped with a rotating molybdenum anode ($\lambda = 0.71073$ Å), a cooling device, and a graphite monochromator. $(PNP)_2[Mo(bdt)_3] \cdot 6 MeOH, C_{96}H_{96}N_2MoO_6P_4S_6, M_r =$ 1785.93 gmol⁻¹, monoclinic, C2/c, a = 22.901(14), b = 16.245(8), c = 25.800(13) Å, β = 113.385(14)°, V = 8810(8) Å³, Z = 4, $\rho_{\text{calcd.}}$ = 1.346 g cm⁻³, $\mu = 0.419$ mm⁻¹. 34636 structure factors (-27 $\leq h \leq$ $27, -19 \le k \le 19, -30 \le l \le 30, 2\theta$ -range 3.2–50.0°) were collected at -100 °C. An empirical absorption correction applied $(T_{\min} =$ 0.921, $T_{\text{max}} = 0.971$) before merging the data gave 7754 unique intensities ($R_{int} = 0.058$). Structure solution was performed with SHELXS,^[16] and the subsequent refinement of 522 parameters against F^2 with 7754 unique intensities [6289 observed intensities I $> 2\sigma(I)$] was conducted with SHELXL.^[17] The anisotropic thermal parameters for all non-hydrogen atoms were refined. Hydrogen atoms were added to the structure model at calculated positions. Final residuals: $R_{all} = 0.0600$, $R_{obs} = 0.0460$, $R_{w,obs} = 0.1182$, GOF = 1.106. The molybdenum atom resides on a special position, namely, a twofold axis which bisects one of the benzene-1,2-dithiolato ligands. The asymmetric unit contains one half [Mo^{IV}(bdt)₃]²⁻ anion, one PNP⁺ cation, and three molecules of MeOH.

X-ray Crystallographic Study of (PNP)[2]: A suitable crystal $(0.48 \times 0.08 \times 0.02 \text{ mm}^3)$ was mounted on a Bruker AXS APEX diffractometer equipped with a rotating molybdenum anode (λ = 0.71073 Å), a cooling device, and a graphite monochromator. $(PNP)[Mo(bdt)_3], C_{54}H_{42}MoNP_2S_6, M_r = 1055.13 \text{ gmol}^{-1}, \text{triclinic},$ $P\bar{1}, a = 11.036(1), b = 13.882(2), c = 16.041(2) \text{ Å}, a = 87.969(3),$ $\beta = 75.861(3), \gamma = 87.512(3)^{\circ}, V = 2380.0(5) \text{ Å}^3, Z = 2, \rho_{\text{calcd.}} =$ 1.472 g cm⁻³, $\mu = 0.645$ mm⁻¹. 19324 structure factors (-13 $\leq h \leq$ 13, $-16 \le k \le 16$, $-19 \le l \le 19$, 20-range 3.0–50.0°) were collected at -120 °C. An empirical absorption correction applied (T_{\min} = 0.747, $T_{\text{max}} = 0.987$) before merging the data gave 8382 unique intensities ($R_{int} = 0.035$). Structure solution was performed with SHELXS,^[16] and subsequent refinement of 577 parameters against F^2 with 8382 unique intensities [6757 observed intensities $I > 2\sigma(I)$] was conducted with SHELXL.^[17] The anisotropic thermal parameters for all non-hydrogen atoms were refined. Hydrogen atoms were added to the structure model at calculated positions. Final residuals: $R_{all} = 0.0476$, $R_{obs} = 0.0335$, $R_{w,obs} = 0.0757$, GOF = 1.007. The asymmetric unit contains one molecule of (PNP)[Mo(bdt)₃].

CCDC-260986 (for $(PNP)_2[Mo^{IV}(bdt)_3]$ -6 MeOH) and CCDC-260987 (for $(PNP)[Mo^V(bdt)_3]$) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgments

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- a) R. Eisenberg, J. A. Ibers, J. Am. Chem. Soc. 1965, 87, 3776– 3778; b) R. Eisenberg, J. A. Ibers, Inorg. Chem. 1966, 5, 411– 416.
- [2] a) D. L. Kepert, Inorganic Stereochemistry; Inorganic Chemistry Concepts 6; Springer Verlag: Berlin, 1982, chapter 8; b) D. L. Kepert, Progr. Inorg. Chem. 1977, 23, 1–65; c) G. N. Schrauzer, V. P. Mayweg, J. Am. Chem. Soc. 1966, 88, 3235–3242; d) E. I. Stiefel, R. Eisenberg, R. C. Rosenberg, H. B. Gray, J. Am. Chem. Soc. 1966, 88, 2956–2966.
- [3] H. V. Huynh, T. Lügger, F. E. Hahn, Eur. J. Inorg. Chem. 2002, 3007–3009.
- [4] a) T. E. Burrow, R. H. Morris, A. Hills, D. L. Hughes, R. L. Richards, *Acta Crystallogr. Sect. C* 1993, 49, 1591–1594; b) F. Knoch, D. Sellmann, W. Kern, *Z. Kristallogr.* 1992, 205, 300–302.
- [5] C. Lorber, J. P. Donahue, C. A. Goddard, E. Nordlander, R. H. Holm, J. Am. Chem. Soc. 1998, 120, 8102–8112.

- [6] a) A. Cervilla, E. Llopis, D. Marco, F. Perez, *Inorg. Chem.* 2001, 40, 6525–6528; b) D. Sellmann, L. Zapf, Z. Naturforsch. *Teil B* 1985, 40, 380–388.
- [7] M. Cowie, M. J. Bennett, Inorg. Chem. 1976, 15, 1584-1589.
- [8] M. Cowie, M. J. Bennett, Inorg. Chem. 1976, 15, 1595–1603.
- [9] M. Cowie, M. J. Bennett, Inorg. Chem. 1976, 15, 1589-1595.
- [10] a) T. J. McMurry, M. W. Hossaini, T. M. Garrett, F. E. Hahn,
 Z. E. Reyes, K. N. Raymond, J. Am. Chem. Soc. 1987, 109,
 7196–7198; b) T. B. Karpishin, T. D. P. Stack, K. N. Raymond,
 J. Am. Chem. Soc. 1993, 115, 182–192.
- [11] J. L. Martin, J. Takats, Can. J. Chem. 1989, 67, 1914–1923.
- [12] a) P. Gosh, A. Begum, D. Herebian, E. Bothe, K. Hildenbrand, T. Weyhermüller, K. Wieghardt, *Angew. Chem.* 2003, *115*, 581– 585; *Angew. Chem. Int. Ed.* 2003, *42*, 563–567; b) K. Ray, T. Weyhermüller, A. Goossens, M. W. J. Craje, K. Wieghardt, *Inorg. Chem.* 2003, *42*, 4082–4087; c) V. Bachler, G. Olbrich, F. Neese, K. Wieghardt, *Inorg. Chem.* 2002, *41*, 4179–4193.
- [13] E. Larsen, G. N. La Mar, B. E. Wagner, J. E. Park, R. H. Holm, *Inorg. Chem.* 1972, 11, 2652–2668.
- [14] S. Campbell, S. Harris, Inorg. Chem. 1996, 35, 3285–3288.
- [15] C. G. Pierpont, C. W. Lange, Prog. Inorg. Chem. 1994, 41, 331– 442.
- [16] G. M. Sheldrick, SHELXS-97, Acta Crystallogr. Sect. A 1990, 46, 467–473.
- [17] G. M. Sheldrick, SHELXL-97, University of Göttingen, 1997. Received: January 26, 2005

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